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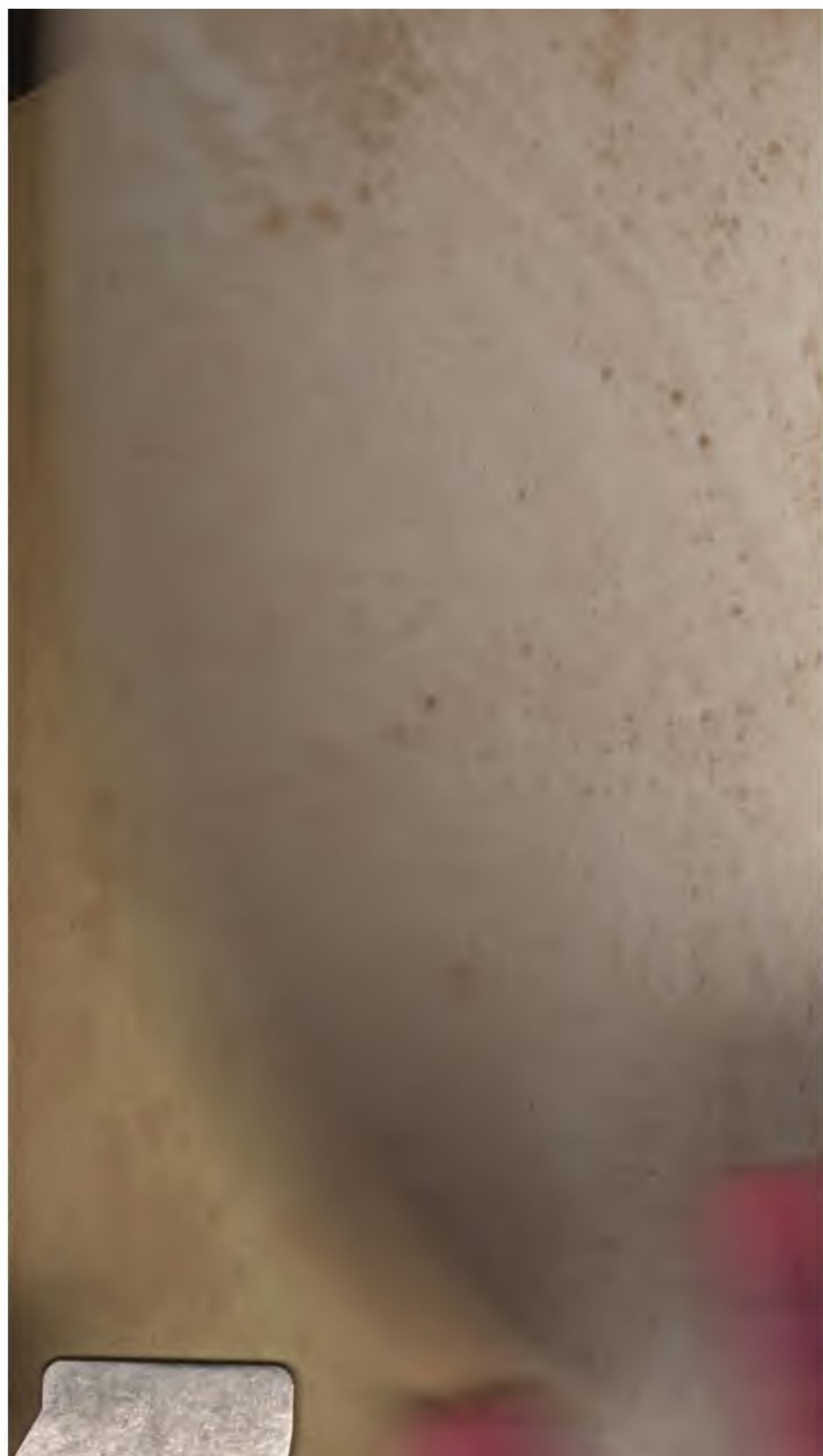
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By WILLIAM GREGORY, M.D., F.R.S.E.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH, AND
AUTHOR OF "HANDBOOK OF INORGANIC CHEMISTRY."

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TO THE
MEMBERS
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AMERICAN ASSOCIATION
FOR
THE ADVANCEMENT OF SCIENCE,
THIS
American Edition
OF
DR. GREGORY'S INORGANIC CHEMISTRY
IS INSCRIBED.

NOTE BY THE AMERICAN EDITOR.

PERHAPS the greatest difficulty to be encountered in the getting up of an elementary work upon Chemistry, at the present day, is not what to put in, but what to leave out. The indefatigable industry of chemists has resulted in the accumulation of such a vast mass of knowledge, such a formidable array of isolated facts, that the author of an elementary work like this, is indeed greatly perplexed to select that which is most appropriate. The editor, even in the preparation of the Supplement to this work, has encountered this difficulty in all of its significance. With such a work before him as the twelve large, closely-printed volumes of Gmelin; with ponderous folios upon physiological and pathological chemistry, and volumes upon this science in its relations to agriculture, technology, and to the growth, products, changes, and decay of animals and plants in general, how is matter to be selected and methodically arranged, suitable to a small work upon the comprehensive subject of Organic Chemistry in general? None but a chemist can, perhaps, comprehend the difficulty of the task, not only of selecting the most appropriate matter, but of arranging it in scientific order.

Even now the profoundest chemical philosophers of the age are contending for two theories respecting chemical combination, which are not at all similar to each other,—proving conclusively that we are yet ignorant of the true manner in which organic molecules are arranged. For instance, such well-known substances as ether and alcohol are still the subject of able controversy between the most experienced chemists of the age—Liebig and Berzelius on the one side, and Dumas and Boullay on the other. According to the latter, ether is a compound of etherine and water = $C_4 H_{10} Aq$, while alcohol is one eq. of etherine and two of water = $C_4 H_{10} 2 Aq$. The former contend that ether is formed of the radical Ethyle

(C, H,) and O, being the oxide of ethyle; and that alcohol is the hydrated oxide of ethyle = C, H₂, O, Aq. It is not probable that water, as such, exists in either alcohol or ether, and that they are not hydrates, or they would yield this water to quicklime or to baryta, which is not the case. Nor is either converted into alcohol by solution in water. Thus we perceive that the chemical world is divided into two parties, one of which accounts for organic combinations upon the RADICAL THEORY, while the other, with equal ability, adopts the NEUCLEUS THEORY.

If we are not yet cognisant of the rational formula of a compound, then we are not prepared to place it in its undeviating position in a scientific arrangement of organic compounds. With these considerations uppermost in our mind, we have discarded the idea we at first conceived, of attempting a scientific arrangement of the substances we have presented in the Supplement. This can best be done after it shall be settled whether the Radical or the Neucleus Theory be the correct one, or whether the true one may not prove to be an intermediate one between the two.

Professor Gregory has attempted a methodical and scientific arrangement of the products and theories of Organic Chemistry in the work we present to the student, and perhaps his arrangement is as scientific an exposition of the doctrines of the science as it is possible to adduce in its present state. The arrangement is as unexceptionable as any that is before the public, and if the Radical Theory be the true one, is decidedly the best in existence. The day, we think, is rapidly approaching when we shall be enabled to place the many facts in chemistry in their proper places. The discoveries of the homologous series of bodies, when still further perfected, will enable us, perhaps, to give the vast mass of chemical facts so lately discovered, "a local habitation and a name;" to arrange them in such a correlated series as will accord with the great scheme of the Creator in the building up of the thousands of organic forms, and their products, so prolifically strewn about us.

The hope is strong within us, that even the next edition of this volume—so rapid is the progress of chemistry—may contain the groundwork of the great desideratum sought for among chemists, viz: that of precision and perfection in the arrangement of the enormous mass of chemical facts now accumulated upon our hands.

In conclusion, the editor would remark, that it is his regret that space was not allowed him for the insertion of much matter equally important as that given. But were the space granted commensurate with the importance and number of the new facts discovered of late, through the indefatigable labors of the host of American and European chemists, this volume would have increased to several times its present size, without further contributing to the thorough comprehension of the elements of Organic Chemistry. Still, although not able to present all the interesting facts connected with our subject, the student will find that the latest discoveries are not passed over without notice, although they are necessarily condensed as much as would be consistent with a thorough comprehension of them. A brief notice of several non-crystallisable salts was introduced in the former edition of this work by the editor. These salts are allowed to remain in this edition, although they really belong to that class of empirical preparations the analogue of which will be found in the "Citrate of quinine and iron," so extensively used by the medical profession. Although not really true salts, still they are valuable and elegant combinations, and consequently are still retained.

NEW YORK, October, 1856.

ORGANIC CHEMISTRY.

INTRODUCTORY.

ORGANIC CHEMISTRY is so called because it treats of the substances which form the structure of organized beings, and of their products, whether animal or vegetable. It has long been known, that all organized structures, as well as all the substances formed in or by these, are, in great part, composed of a very limited number of elements; insomuch that a large proportion of them may be described as consisting, almost exclusively, of only four simple substances, namely, Carbon, Hydrogen, Oxygen, and Nitrogen.

But while these four elements undoubtedly constitute the chief part of all organized tissues, and while such products as woody fibre, sugar, starch, gum, fat, oils, and many organic acids, contain only the first three, that is, carbon, hydrogen, and oxygen, we must not forget that other elements occur in the organized kingdoms of nature; some of them, such as those of Phosphate of Lime, in large quantity; and all, whether they occur in smaller or greater proportion, as truly essential to animal and vegetable life, as the four elements above mentioned, the predominance of which characterizes the organic world.

Thus, no plant can grow, or form cells, or even fibre, without the presence of certain mineral or saline compounds, which are derived from the soil, and which when the plant is burned, constitute its ashes. These are, potash, soda, lime, magnesia, with occasionally oxides of iron and manganese, as bases; and silicic acid, phosphoric acid, sulphuric acid, chlorine, fluorine, and iodine, as acids and acid-radicals.

Again, the juices of all plants, and more especially their roots and seeds, contain some one or more of the compounds known by the names of albumen, fibrine, and caseine. Now these compounds contain small, but absolutely essential proportions of sulphur and phosphorus, besides earthy and alkaline phosphates.

Lastly, the bones of animals contain not only phosphate of lime, but also phosphate of magnesia and fluoride of calcium, both in very considerable quantity; and iron is an unfailing constituent of blood.

To the four elements first mentioned, as constituting the chief mass of organic substances, we must therefore add, as no less

essential, although for the most part in smaller proportion, the following metalloids — Chlorine, Fluorine, Sulphur, Phosphorus, and Silicon ; and the following metals — Potassium, Sodium, Calcium, Magnesium, Iron, and occasionally Manganese.

It thus appears that the fourteen or fifteen elements which constitute the chief mass of the mineral or inorganic world, are almost the same which occur in organized matter : the difference being chiefly this, that in inorganic nature the *predominant* elements, nearly in the order of their abundance, are Oxygen, Hydrogen, Nitrogen, Silicon, Chlorine, Sodium, Aluminum, Carbon, and Iron ; after which follow Potassium, Calcium, Magnesium, Sulphur, Phosphorus, and Fluorine : while in the organic department the order is nearly as follows — Carbon, Oxygen, Hydrogen, Nitrogen, Potassium, Calcium, Phosphorus, Silicon, Sulphur, Sodium, Magnesium, Chlorine, Iron, and Fluorine. Aluminum, so very abundant in the mineral kingdom, hardly ever occurs in organic compounds, and when it does occur, is perhaps accidental.

The above considerations are sufficient to show, that there is no essential distinction to be made between organic and inorganic chemistry, founded on the nature of the elements concerned.

Neither is there any such distinction to be pointed out in regard to the laws of combination and decomposition which prevail in these different departments of chemistry ; for we find the same affinities operating ; and although organized tissues, and their products, have, in general, a more complicated constitution than inorganic compounds, containing a larger number of equivalents of their elements, and consequently having much higher atomic weights, we cannot consider such characters as forming a valid ground of distinction.

But while we should find it very difficult, if not impossible, to draw the line between inorganic and organic chemistry on scientific principles, we may still recognize, for convenience' sake, a certain distinction, founded, first, on the origin of substances, whether animal and vegetable, or mineral ; and secondly, on the uniform predominance of carbon in animal and vegetable matter.

In reference to the first point, it is to be observed, that, although the elements concerned are those common to the inorganic and organic kingdoms, the compounds which constitute the latter are formed under peculiar circumstances, such as, for the most part, cannot be imitated in our experiments.

It is true that chemistry has succeeded, in some cases, in forming artificially certain compounds which occur as products of organic life, such as urea, formic acid, and oil of spiræa. But, in the first place, most, if not all of these, require for their production the aid of an organic product : thus, formic acid is produced from starch, oil of spiræa from salicine ; and although urea may be obtained from cyanic acid and ammonia, it is doubtful if either

cyanogen or ammonia can be obtained except from organic compounds, directly or indirectly. Secondly, it is particularly to be noticed, that we have not yet succeeded in forming, artificially, either an organized tissue, or even any one of the compounds (albumen, &c.) of which such tissues are made. Those organic compounds which have been artificially formed, are invariably *products of decomposition*, or, in other words, the excretions or secretions of organized bodies: and are far less complex in their constitution than organized structures.

From these facts we draw the conclusion, that certain circumstances, of which the most important is the *vital force*, so modify the play of affinities in organized beings, as to produce the compounds usually termed organic, which, so far as they are capable of entering into the composition of tissues, cannot be imitated by art.

In regard to the second peculiarity of organic compounds, namely, the predominance of carbon in their composition, we observe that, as this carbon is united to the three gases, oxygen, hydrogen, and nitrogen, with each of which it forms gaseous compounds, and as, further, the latter elements, among themselves, form compounds, such as water and ammonia, which are also volatile, so the action of heat on organic compounds is characteristic; producing *combustion* of all, save the ashes, when there is free access of air; and *charring* them, or, in other words, causing the separation of part of their carbon, in close vessels, while the greater part is dissipated in the form of volatile products.

Here, then, we have a ready test of organic matter, which is so characteristic, that we might almost define organic chemistry as the chemistry of such compounds as are charred when heated to redness in close vessels. There are very few substances, indeed, of organic origin, which do not exhibit this character.

Organic chemistry has been defined as the chemistry of compound radicals; but, although we must admit the existence of many such radicals in organic chemistry, we cannot adopt this definition in contradistinction to that of inorganic chemistry, as the chemistry of simple radicals, because the recent progress of science has led, or almost compelled us to admit the existence of compound radicals in inorganic chemistry, as has been explained in the first part of this work.

It is, perhaps, worth while to point out, that all the organic compound radicals hitherto established, or supposed to exist, are compounds of carbon, if we except amidogen (see p. 85), which contains only hydrogen and nitrogen.

It is also proper here to state, that, under the name of organic compounds, many substances are treated of which do not occur in nature, but which have been obtained by subjecting true organic products to various influences: to that, for example, of heat, as in

what is called the destructive distillation, which yields such substances as naphtha, naphthaline, &c. ; or to the action of chlorine or bromine, of sulphuric or nitric acids, of alcalies, &c., by all which means whole series of new compounds are obtained. Lastly, some very interesting and important compounds are included under the term organic, which arise from the addition of elements not naturally occurring in the organic kingdom ; as for example, cacodyle and its compounds, which contain arsenic as an essential constituent ; and the very singular bases in which platinum is added to some of the usual elements of organic alcalies.

But while, as has just been stated, compound radicals are not exclusively characteristic of organic chemistry, we may still derive great assistance from attending to the compound radicals of organic chemistry. For while we admit the existence of such radicals in inorganic chemistry, along with simple radicals, we must bear in mind that all the organic radicals as yet discovered are compound, and many of them exceedingly complex, containing three or four elements.

It is true that we are not yet acquainted with the radicals of a very large proportion of organic compounds ; such as the principal organic acids, the organic alcalies, &c. But the known organic radicals furnish us with the means of classifying many most important substances, just as we classify the compounds of any metalloid or of any metal together. As to those groups or series of organic compounds, the radicals of which are not yet known, we can only class them according to analogies of properties, of composition, or of both.

With these introductory remarks, we shall proceed to consider the known organic compound radicals, and their derivatives.

COMPOUND ORGANIC RADICALS.

A compound radical is a substance which, although containing two or more elements, enters into combination with elementary bodies as if it were itself elementary, and in ordinary circumstances performs exactly the part of an element.

In the first part of this work, we have already admitted as probable the existence of inorganic compound radicals, such as SO_4 , the radical of sulphuric acid, and NO_3 , that of nitric acid. These bodies are, in their relations to others, entirely analogous to chlorine. Thus we may represent the acids of these three radicals, with their potassium and silver salts, as follows :

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine	$\text{H} + \text{Cl}$	$\text{K} + \text{Cl}$	$\text{Ag} + \text{Cl}$
	SO_4	$\text{H} + \text{SO}_4$	$\text{K} + \text{SO}_4$	$\text{Ag} + \text{SO}_4$
	NO_3	$\text{H} + \text{NO}_3$	$\text{K} + \text{NO}_3$	$\text{Ag} + \text{NO}_3$

The compound inorganic radicals, SO_2 and NO_2 , therefore, perform exactly the part of a metalloid of the group of chlorine.

But there have also been briefly mentioned, in the First Part, certain compound organic radicals, which not only exhibit, in their relations, characters analogous to those of chlorine, but actually exist, like chlorine, in the separate state, which is not the case with SO_2 and NO_2 , these latter being only known in combination.

The organic radicals here alluded to are cyanogen, $\text{C}_2\text{N} = \text{Cy}$ and mellone $\text{C}_2\text{N}_4 = \text{Me}$ (see Part I., p. 140). They may be compared to chlorine exactly like the two above-mentioned inorganic compound radicals. Thus,

	Acid.	Potassium Salt.	Silver Salt.
Radicals $\left\{ \begin{array}{l} \text{Chlorine Cl} \\ \text{Cyanogen Cy} \\ \text{Mellone Me} \end{array} \right.$	$\text{H} + \text{Cl}$	$\text{K} + \text{Cl}$	$\text{Ag} + \text{Cl}$
	$\text{H} + \text{Cy}$	$\text{K} + \text{Cy}$	$\text{Ag} + \text{Cy}$
	$\text{H} + \text{Me}$	$\text{K} + \text{Me}$	$\text{Ag} + \text{Me}$

Cyanogen and mellone are, therefore, radicals of the nature of the chlorine group of metalloids. The bisulphide of cyanogen, or sulphocyanogen, $\text{C}_2\text{N}_2\text{S}_2 = \text{CyS}_2$, although it contains three elements, plays the same part as chlorine or cyanogen, and forms with hydrogen the acid $\text{H} + \text{CyS}_2$, with potassium the salt $\text{K} + \text{CyS}_2$, and with silver the salt $\text{Ag} + \text{CyS}_2$.

Some compound organic radicals appear more analogous to the combustible group of metalloids, that is, to carbon, sulphur, or phosphorus; inasmuch as they form acids with oxygen, or rather with the elements of water like those metalloids, and are besides capable of entering into combination with chlorine, iodine, &c. Such radicals are carbonic oxide, CO , or rather an isomeric modification of it, C_2O_2 ; acetylene, C_2H_2 ; and formyle, C_2H . Each of these may be viewed as the radical of a powerful acid; for $\text{C}_2\text{O}_2 + \text{O} = \text{C}_2\text{O}_3$ is dry oxalic acid; $\text{C}_2\text{H}_2 + \text{O}_2$ is dry acetic acid; and $\text{C}_2\text{H} + \text{O}_2$ is dry formic acid. Again, the first forms with chlorine the compound $\text{C}_2\text{O}_2 + \text{Cl}_2$, called phosgene gas or chlorocarbonic acid, while the two others yield $\text{C}_2\text{H}_2 + \text{Cl}_2$, the chloride of acetylene, and $\text{C}_2\text{H} + \text{Cl}_2$, the perchloride of formyle.

Further, there are organic compound radicals which play the part of metals, forming salts with chlorine, iodine, sulphur, cyanogen, &c., and yielding, with oxygen, compounds possessing basic properties analogous to those of metallic oxides. Such radicals are ethyle, C_2H_5 ; methyle, C_2H_3 ; and cacodyle, $\text{C}_4\text{H}_5\text{As}_2$.

Radicals.	Oxygen Compound.	Chlorine Compound.	Cyanogen Compound.	Sulphur Compound.
Ethyle $\text{C}_2\text{H}_5 = \text{Ae}$	AeO	AeCl	AeCy	AeS
Methyle $\text{C}_2\text{H}_3 = \text{Mt}$	MtO	MtCl	MtCy	MtS
Cacodyle $\text{C}_4\text{H}_5\text{As}_2 = \text{Kd}$	KdO	KdCl	KdCy	KdS

Lastly, there are some compound organic radicals, which partake of the characters of the two last groups, forming, like the acetylene group, acids and not bases with oxygen; but yielding, with chlorine, sulphur, cyanogen, &c., compounds analogous to those formed by the ethylene group. To this division belong benzoyle, $C^6H_5O_2 = Bz$; cinnamyle, $C^6H_5O_2 = Ci$; and several others. Benzoyle and cinnamyle, with the addition of oxygen and the elements of water, produce benzoic acid, BzO, H_2O , and cinnamic acid, CiO, H_2O . This group is characterized by forming with hydrogen certain essential oils. Thus, benzoyle yields, with hydrogen, the essential oil of bitter almonds, BzH ; cinnamyle yields the oil of cinnamon, CiH ; and salicylene, $C^6H_5O_4 = Sa$; another radical of this group, forms, with hydrogen, the oil of spiræa, SaH .

These brief statements will serve to show that there are different kinds of groups of compound radicals, just as there are of simple ones; and further, that these compound radicals exhibit a very remarkable tendency to combine with simple radicals, and, in fact, to act the part of elementary bodies. And let us here bear in mind that the only real difference, in this point of view, between cyanogen and chlorine is this, that in the case of the former we can prove the radical to be compound, while we cannot as yet do this in the case of the latter. But, as formerly pointed out, we call chlorine, and indeed all other elements simple, only because we have not been able to show them to be compound; without having any certainty that they are really and absolutely simple. If we could not resolve cyanogen into carbon and nitrogen, we should be compelled to add it to the list of elements.

But although compound radicals usually act toward other bodies as if simple, and consequently combine generally with simple substances, they are also capable of uniting with each other. In fact, this is but another proof of their close resemblance to elementary bodies in their relation; for as simple metals, such as potassium and silver, unite with cyanogen just as with chlorine, so also such compound radicals as are analogous to metals can combine with cyanogen, itself a compound radical. Thus ethylene, methylene, benzoyle, and cacodylene all combine with cyanogen, yielding compounds formed of two organic radicals, one playing the part of a metalloid, the other that of a metal.

Compounds of this nature furnish the very best proof and illustration of the advantages which we derive from the doctrine of compound radicals, acting like elements, whenever we are justified by facts in adopting and applying it. Thus a compound has been formed by the mutual action of a compound of cacodylene and a compound of cyanogen, the analysis of which proves that it contains carbon, hydrogen, nitrogen, and arsenic, in the relative proportions indicated by the formula $C_6A_2NAs_2$. What view

are we to take of such a formula? and if we look on the compound as one formed of these four elements indiscriminately united, how are we to retain such an insulated fact in the memory? But if, on the other hand, we view it as the cyanide of cacodyle, $= C_4 H_8 As_2 + C_2 N$, or, using the abbreviated notation appropriate to compound radicals, Kd Cy, we are at once enabled to retain the composition and chemical relations of the compound. Moreover, when we find that the radical, Kd ($= C_4 H_8 As_2$) exists in a separate form, and that it forms, with oxygen, two compounds, Kd O and Kd O₂; with chlorine, Kd Cl; with sulphur, Kd S; and that, in short, it plays the part of a metal in all its compounds, and may in fact be separated from some of these by metals having stronger affinities than itself, we are supplied with an idea which serves to connect and to fix all these and many more analogous facts in the memory.

When we further observe, to pursue the same example, that the cyanide of cacodyle, Kd Cy, when acted on by hydrochloric acid, gives rise to hydrocyanic acid and chloride of cacodyle; and that, when acted on by potash, it yields cyanide of potassium and oxide of cacodyle, we acquire so many additional proofs of the entire analogy between simple and compound radicals in their relation to other bodies. For the two changes or reactions above mentioned are expressed by the equations, $Kd Cy + H Cl = Kd Cl + H Cy$; and $Kd Cy + K O = Kd O + K Cy$; and these equations are exactly similar to those which occur most frequently in inorganic chemistry.

The facts already ascertained with regard to those compound organic radicals, whose existence has been either established, or rendered highly probable, entitle us to conclude that all organic compounds contain one or more organic radicals, combined either with each other, or with elementary radicals. In studying therefore, any organic product, one chief object is to determine what organic radical or radicals it contains, since the knowledge of these at once gives us a means of classification.

Thus alcohol, on the theory of compound radicals, is considered as the hydrated oxide of ethyle; ethyle being an organic radical, $C_4 H_8$. So that alcohol, $C_4 H_8 O_2$ is more accurately represented as $(C_4 H_8) O + H O$; or if we represent ethyle, $C_4 H_8$, by Ae, then alcohol becomes Ae O, H O, hydrated oxide of ethyle; perfectly analogous to K O, H O, hydrated oxide of potassium, or caustic potash.

Again, benzoic ether, $C^{18} H^{10} O_4$, is viewed as benzoate of oxide of ethyle, $C_4 H_8 O + C^{14} H_6 O_3$; or more briefly, Ae O + Bz O. Here we have the basic oxide of one radical united with the acid oxide of another.

It was often by means of thus tracing the different organic radicals, that we are enabled to explain the very numerous cases of

isomerism, which occur in organic chemistry. Thus, the following compounds have the same composition in 100 parts :

Aldehyde	$C_4 H_4 O_2$
Acetic Ether	$C_4 H_4 O_4$
Butyric Acid	$C_4 H_4 O_4$

Now, aldehyde is considered to be the hydrated protoxide of acetylene, $(C_2 H_2) O + H O$; or, abbreviated, $Ac O, H O$. Again, acetic ether is acetate of oxide of ethylene, $C_2 H_2 O + (C_2 H_2) O_2$; or shortly, $Ac O, Ac O_2$; the dry acetic acid, $Ac O_2 = (C_2 H_2) O_2$, being a peroxide of the same radical, acetylene, $(C_2 H_2 = Ac)$ of which aldehyde is the protoxide. Lastly, butyric acid is considered (on the older view of acids,) as a hydrated acid, a compound of water with dry butyric acid ; thus, $H O + C_2 H_7 O_2$.

It is true, that, in the latter case, we are not yet acquainted with the true radical of butyric acid ; but we cannot doubt that, like acetic acid, it does contain a radical. These three compounds, therefore, may now be represented and distinguished as follows :

Empirical Formula.	Rational Formula.
Aldehyde	$C_4 H_4 O_2 = (C_2 H_2) O + H O$
Acetic Ether	$C_4 H_4 O_4 = (C_2 H_2) O + (C_2 H_2) O_2$
Butyric Acid	$C_4 H_4 O_4 = C_2 H_7 O_2 + H O$

Even in those cases in which the composition of the radical is not known, or not known with certainty, we can often trace the radical with much probability. Thus, dry oxalic acid, $C_2 O_2$, and dry mellitic acid, $C_6 O_2$, may be viewed as different compounds of the simple radical carbon, the latter containing just twice the proportion of carbon to the same quantity of oxygen that the former does. This is merely stated by way of illustration : for, it is at least equally probable that the true radical of oxalic acid is $C_2 O_2$.

But in the following four acids we may trace, theoretically, the same compound radical, namely, formyle, $=C_2 H$, in combination with the different proportions of oxygen. Here $C_2 H$ is also represented by Fo .

Formic Acid	$(C_2 H) + O_2 = Fo O_2$
Succinic Acid	$C_4 H_2 O_2 = 2 (C_2 H) + O_2 = Fo_2 O_2$
Malic Acid	$C_4 H_2 O_4 = 2 (C_2 H) + O_4 = Fo_2 O_4$
Racemic Acid	$C_4 H_2 O_4 = 2 (C_2 H) + O_4 = Fo_2 O_4$

These relations, although as yet only to be traced in the formulae, are yet not without interest, and may, at all events, serve to aid the memory.

In like manner it may be observed, that the following acids all contain, as hydrates, 4 eq. of oxygen ; and all likewise the same number of eqs. of carbon as of hydrogen.

1. Acetic Acid	$C_2 H_4 O_4 = C_2 H_3 O_3, H O$
2. Metacetic Acid	$C_3 H_6 O_4 = C_3 H_5 O_3, H O$
3. Butyric Acid	$C_4 H_8 O_4 = C_4 H_7 O_3, H O$
4. Valerianic Acid	$C_{10} H_{10} O_4 = C_{10} H_9 O_3, H O$
5. Carproic Acid	$C_{12} H_{12} O_4 = C_{12} H_{11} O_3, H O$
6. Cœnanthyllic Acid	$C_{14} H_{14} O_4 = C_{14} H_{13} O_3, H O$
7. Caprylic Acid	$C_{16} H_{16} O_4 = C_{16} H_{15} O_3, H O$
8. Pelargonic Acid	$C_{18} H_{18} O_4 = C_{18} H_{17} O_3, H O$
9. Capric Acid	$C_{20} H_{20} O_4 = C_{20} H_{19} O_3, H O$
10. * * * * *	* * * * *
11. Lauric Acid	$C_{24} H_{24} O_4 = C_{24} H_{23} O_3, H O$
12. Cocinic Acid	$C_{26} H_{26} O_4 = C_{26} H_{25} O_3, H O$
13. Myristic Acid	$C_{28} H_{28} O_4 = C_{28} H_{27} O_3, H O$
14. * * * * *	* * * * *
15. Palmitic and Ethalic Acids	$C_{32} H_{32} O_4 = C_{32} H_{31} O_3, H O$
16. Margaric Acid	$C_{34} H_{34} O_4 = C_{34} H_{33} O_3, H O$

Here we may suppose the radical of the first acid to have been changed by the successive additions of 2, 4, 6, 10, or 20, or more eq. of carbon or hydrogen, the oxygen remaining unchanged. Or we may as readily suppose, one of these acids, by losing oxygen, to pass into another. Thus we may either conceive butyric acid to be formed from acetic acid by the addition of $C_2 H_4$; or acetic acid to give rise to butyric acid by losing half its oxygen; for $2(C_2 H_4 O_4) = C_4 H_8 O_8$; and $C_4 H_8 O_8 - O_4 = C_4 H_8 O_4$.

When compound organic radicals, or their compounds, are subjected to powerful decomposing agencies, they tend to produce new and complex radicals. Thus, when alcohol, the hydrated oxide of ethyle, is oxidized, it gives rise to aldehyde and acetic acid, which are compounds of acetylene, $C_2 H_2$, a less complex radical than ethyle, $C_2 H_6$. Further, when organic compounds are decomposed by a strong heat, they tend to produce compounds of simple radicals, such as carbon or hydrogen, or, at most, of the least complex radicals, such as cyanogen, $C_2 N_2$, and amidogen, $N H_3$. These are principles of very general application.

It may here be observed, that while in such cases as the supposed conversion of acetic into butyric acid, by the loss of half its oxygen, the change is from a less complex to a more complex organic compound, and while we can hardly doubt the possibility of such a result, yet the *oxidation* of a compound radical, that is, the addition of oxygen, appears always to produce less complex radicals or compounds.

It is often urged, as an argument against the doctrine of compound radicals, that these supposed radicals are entirely imaginary and cannot be produced. Now, it is true, that a large proportion of those, whose existence is best attested, have not yet been obtained in the uncombined state; and it is even probable that some of them are only capable of existing, or rather, of being preserved, when combined. But the argument founded on this fact has no

cogeny; for, in the first place, some organic radicals, such as cyanogen and cacodyle, are well-known in the separate state. Now cyanogen and cacodyle are, in all their relations, exactly analogous, the former to chlorine, the latter to a metal; and, if we were unable to demonstrate their compound nature, their chemical relations would compel us to classify cyanogen as an element along with chlorine, and cacodyle along with the metals; and when we see whole series of organic compounds, in all respects analogous to those of cyanogen and cacodyle, we are entitled logically to draw the conclusion that these compounds contain similar compound radicals, even although we cannot isolate them. Secondly, in every chemical theory yet broached, many substances are admitted whose existence cannot be directly proved. Thus the so-called anhydrous organic acids are, almost without exception, unknown in the separate state; they are equally imaginary with the radicals, whose existence is doubted. Nay, many inorganic acids are equally hypothetical. Anhydrous nitric acid has never been seen; and although there are reasons for doubting its existence, yet no one doubts the existence of hyposulphurous acid, which yet has never been separated, either as a hydrate or in the anhydrous state.

We conclude, therefore, that organic compound radicals exist, and generally play the part of elements; and we shall avail ourselves of their existence, as far as it is established, to facilitate the study, the classification, and the retention in the memory, of organic compounds.

THEORY OF CHEMICAL TYPES. — DOCTRINE OF SUBSTITUTION.

The original and ingenious researches of Laurent have led to the adoption of what is called the Theory of Types, and the Law or Doctrine of Substitution, which have been supported, and in a great measure established, by Dumas and other distinguished experimenters of the French school. The views of Laurent and of Dumas were for a time vehemently opposed by some chemists, especially by Barzelius and Liebig; but although they have in some points been modified and restricted, the progress of discovery has gradually led to their general reception, so that recently some of the most striking illustrations and proofs of the law of substitution have been discovered by Dr. Hoffman, assistant to Baron Liebig, and working under his eye.

As the subject is, therefore, no longer purely controversial, it would be wrong to omit it in an elementary work, much more especially as the doctrine has now taken such a form as to facilitate very much the study of organic compounds and of their metamorphoses.

It is not easy to define a chemical type; but in inorganic chemistry we may say, for example, that hydrochloric acid, H Cl , is the

type of a very numerous class of acids, the character of which is, that they contain hydrogen united to a salt radical.

If for chlorine we substitute iodine, bromine, &c., or even cyanogen, the type remains unchanged, the compound is still an acid, analogous to that which was selected as the type.

Again, common salt, Na Cl, is the type of a very large series of salts, in which a metal is united with a salt radical; and if we substitute potassium, lead or silver for the sodium, the type is unaltered; we obtain a different salt, but still a salt of the type represented by Na Cl.

Here, then, we have the simplest types and the most obvious cases of substitution; when iodine or cyanogen is substituted for chlorine in the acid type; or when potassium, lead, or silver is substituted for sodium in the salt type; in both cases without the loss of the type.

Nay, in the salt type represented by Na Cl, we may not only replace sodium by other metals, but we may also substitute iodine, bromine, &c., or cyanogen, for the chlorine, and still the type will remain unchanged. Iodide of sodium, Na I, bromide of magnesium, Mg Br, and cyanide of silver, Ag Cy, are all as good examples of the salt type represented by Na Cl, as common salt itself is.

It has been proposed, with great propriety by Baudrimont, to employ certain Greek characters, as symbols in representing the formulæ of extensive types or of types in general. I shall, therefore, express the above salt type by the formula Δx , in which Δ stands for any metal or body acting as a metal, and x for chlorine or any other radical of analogous power, such as cyanogen. As hydrogen appears to stand alone in the power of forming acids with bodies of the type x , the acid type above alluded to becomes in its most general form hx .

But while it is very easy to understand the extensive substitutions which may be effected in the case of both elements of the type Δx , yet we observe that in these substitutions the electrical character of the elements is retained; and that as Δ is the positive, and x is the negative element, so they are only replaced, Δ by positive and x by negative elements respectively.

So far as inorganic chemistry is concerned, the study of types would serve generally to confirm and establish the electro-chemical theory. At all events, we are not as yet acquainted with many exceptions to it; we do not usually find oxygen or chlorine occupying the place of Δ in a compound, or a metal playing the part of x . Even in inorganic chemistry, however, there are some examples of such interchanges. Manganese in manganic acid, $Mn O_3$, and chromium in chromic acid, $Cr O_3$, obviously represent the sulphur in sulphuric acid; and the manganese in hypermanganic acid, $Mn_2 O_7$ represents the chlorine in perchloric acid, $Cl O_7$; while, in its other compounds, manganese acts as a metal.

But the researches of Laurent and Dumas have shown that in organic chemistry the substitution of one element for another, even where the type is retained, is not limited by the electrical character of the elements. Thus, in acetic acid, $\text{H O, C}_4 \text{ H}_3 \text{ O}_3$, the 3 eq. of hydrogen in the anhydrous acid may be replaced by chlorine, giving rise to the compound $\text{H O, C}_4 \text{ Cl}_3 \text{ O}_3$, in which the type is so little affected, that this substance, chloracetic acid, has properties highly analogous to those of acetic acid. Here it is evident that the chlorine performs the same function as the hydrogen which it replaces did; and not, as in hydrochloric acid, an opposite function.

Again, in aldehyde, $(\text{C}_4 \text{ H}_3) \text{ O} + \text{H O}$, the 3 eq. of hydrogen in the radical $\text{C}_4 \text{ H}_3$ may be replaced by 3 eq. of chlorine, and we then have chloral, $(\text{C}_4 \text{ Cl}_3) \text{ O} + \text{H O}$, a body of the same type as aldehyde.

Such cases of substitution of chlorine (iodine, bromine, &c.,) for hydrogen, and even of oxygen for hydrogen, without change of type, are very frequent; and it is this kind of substitution, so adverse to the electro-chemical theory, which is included in the theory of substitutions of Laurent. Those more usual substitutions, where one body is replaced by another of similar electrical character, may be viewed as so many examples of the doctrine of equivalents, the replacing body being equivalent to that for which it is substituted, on the electro-chemical theory.

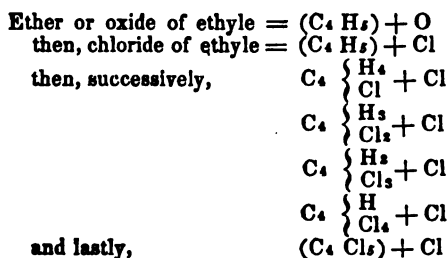
Adopting, then, the views of Laurent, we are compelled to admit that the electro-chemical theory fails when applied to cases of substitution of chlorine for hydrogen, &c., where the type remains unaltered. This is clearly the case in acetic and chloracetic acids; and Hoffman has recently shown that in certain basic organic compounds, hydrogen may be replaced by chlorine, while the new compound retains the basic type and characters. Aldehyde and chloral furnish an example of the same, in a body neither acid nor basic.

Here, then, is a fact of very general occurrence, which not only proves that the electro-chemical theory of combination is inapplicable, at all events in many cases, but also tends to establish a very different view: namely, that the electric character of an element is no permanent or essential property; and that the type or character, or general properties of a compound, depend, not on the *nature*, but solely on the *arrangement* of its elementary atoms; on the way in which they are grouped to form the compound molecule.

The reader will remember that, in the section on Isomorphism, the principle was laid down that the crystalline form of certain types of salts, such as the alum type, as well as many other properties of the compounds having those types, where the result of the *similar grouping of analogous elements*. We now see that,

according to the law of substitution, as deduced from numerous careful observations, similarity of properties, or identity of type, are the result of similarity of grouping, even of elements not analogous, nay, of elements electrically opposed to each other. It is evident, therefore, that the arrangement of the elementary molecules to form the compound molecule is the circumstance on which depend almost exclusively the properties of the compound, or, in other words, the character of the type.

Substitution may be either complete or partial. In chloroacetic acid, and in chloral, the substitution of chlorine for the hydrogen of the radical acetyl $C_2 H_3$ is complete. But when ether $(C_2 H_5)_2 O$ is acted on by chlorine, the substitution takes place by successive steps, one equivalent of hydrogen being replaced at a time, after the oxygen has also been replaced by chlorine. Thus we have, first:



We thus obtain the series of compounds here indicated, in which the hydrogen is gradually replaced by chlorine, until at last we obtain the compound $(C_2 Cl_5)_2 + Cl = C_2 Cl_5 = 2 C_2 Cl_3$, which is the perchloride of carbon.* Most of these compounds have actually been obtained; and it is obvious that they may all be referred to one type. Such a series is called a series of mechanical examples of the type in question, or rather of subtypes retaining the original character although modified.

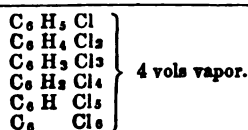
* The action of chlorine upon *Propylene*, as lately got by Cohout, is also a striking illustration of the doctrine of substitution, thus:

Propylene.			
$(C_3 H_6)_2 Cl_2$	boils at 104°	density 1.151	= 4 vols.
$C_3 H_5 Cl_3$	" 170°	" 1.347	= 4 "
$C_3 H_4 Cl_4$	" 195° 200°	" 1.548	= 4 "
$C_3 H_3 Cl_5$	" 220° 225°	" 1.548	= 4 "
$C_3 H_2 Cl_6$	" 240° to 245°	" 1.626	= 4 "
$C_3 H Cl_7$	" 260°	" 1.731	= 4 "
$C_3 Cl_8$	" 280°	" 1.860	= 4 "

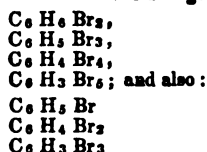
These compounds distilled with alcoholic solution of potassa, yield a new series of homologues:

In some cases, hydrogen has been replaced partly by chlorine, and partly by bromine. Laurent has described two compounds derived from naphthaline by substitution, the empirical formula for both of which is the following:— $C_{10}H_4Cl_3Br$. Yet the properties of these two compounds are quite distinct, and it is certain that this difference of properties must depend on a difference in the arrangement of the elements. Now, in the formation of these two compounds we have a very beautiful proof of the existence of a difference in the arrangement: for one is produced when chlorine acts on the compound called by Laurent bronaphtèse, $C_{10}H_6Br_2$; while the other is formed when bromine is made to act on clonaphtise, $C_{10}H_8Cl_2$. It is obvious that in the first case 2 eq. of hydrogen and 1 eq. of bromine are replaced by chlorine; while in the second, 1 eq. of hydrogen is replaced by bromine. While, therefore, all four compounds may be deduced from the type $C_{10}H_8$, and while both the bromine and chlorine play the part of hydrogen, it is impossible to doubt that each of the 8 eq. of hydrogen has its special place in the compound molecule of the type, and that, in the two empirically identical formulæ above given, the 1 eq. of bromine does not replace the same eq. of hydrogen, and consequently the bromine occupies in the two compounds different positions. The same remark applies to the 3 eq. of chlorine.

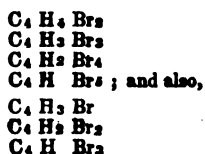
We may illustrate our meaning as follows:—Let $C_{10}H_8$ be the type, and let each of the eqs. of hydrogen have a number attached indicating its place in the typical molecule. We shall then have

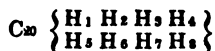


We also get :

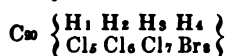


Also the action of bromine and an alcoholic solution of potassa, upon the brominated Dutch liquor, $C_4H_4Br_2$:

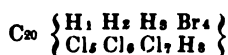




Now, if we represent the two compounds above mentioned in the following manner, we can then conceive the influence of arrangement on the properties of two compounds having the same empirical formula. The first may be



and the second may be



It is only on this principle that we can explain the facts observed by Laurent; and it is easy to see that the above type, $C_{20}H_8$, will admit of innumerable modifications; for even the subtype, $C_{20}H_4Cl_2Br$, is capable of yielding many more than the two above given; and the change of 1 eq. produces a new subtype, equally fertile in new forms.

In fact, Laurent has actually obtained, as will be shown farther on, a very large number of what we have called subtypes, from the type $C_{20}H_8$, which is naphthaline, and has established the same law in reference to many other types.

The preceding observations will, I trust, be found sufficient to convey a clear general notion of the prevalent doctrines of chemical types and of substitution, as applied to organic chemistry. It is evident that the facts of substitution are of great interest, and not only enable us to classify and to remember numerous complex facts, but promise to throw much light on the molecular constitution of compound bodies. But while admitting the importance of the doctrine of substitution, it is necessary to point out that the French chemists appear to have gone too far in assuming that this doctrine is incompatible with that of compound radicals. It is certain that some compound radicals exist, and it is no less certain that by assuming their existence in other cases, we very much facilitate the study of many important series of compounds. Let us, therefore, avail ourselves of that which appears well founded in both doctrines, since there appears to be no reason why the one should be opposed to the other.

THE DECOMPOSITIONS AND METAMORPHOSES OF ORGANIC COMPOUNDS.

Organic compounds, whether actual organized tissues, unorganized products of animal and vegetable life, or new substances artificially produced, are generally characterized by a great proneness to undergo decomposition or metamorphosis. This instability is especially marked in those compounds which contain nitrogen, not only because, containing four elements (in most cases), they

are exposed to more numerous causes of change than such bodies as contain only three (carbon, hydrogen, and oxygen), but also because nitrogen is in its relation to those three elements, the most remarkable element we know. According to the circumstances under which a change is induced, nitrogen may separate uncombined, as in the ultimate analysis of organic substances by combustion with oxide of copper or chromate of lead; or it may combine with oxygen, yielding nitric acid, as in nitrification; or with carbon, yielding the compound radical cyanogen, as when nitrogenized organic matter is ignited with carbonate of potash; or with hydrogen, yielding ammonia, as when nitrogenized organic matter is ignited with hydrated alcalies.

It is easy to see, therefore, that while all organic matter is prone to change, this is especially the case with nitrogenized compounds. In fact, many of these compounds cannot be kept more than a few hours without the commencement of decomposition or metamorphosis, in the shape of putrefaction or fermentation. This kind of metamorphosis will be separately considered hereafter; in the meantime it is important to observe, that when such a compound has entered into a state of decomposition, it acquires the properties of a ferment, that is, it is capable of inducing a similar metamorphosis in another compound, if placed in contact with it.

The true explanation of this fact appears to be, that the particles or molecules of the exciting body or ferment, being in a condition of change, and therefore in motion, communicate to the molecules of the body placed in contact with them an amount of motion sufficient to destroy the balance of the existing affinities; which in organic compounds is easily done, the chemical equilibrium being very unstable; and thus gives rise to a new play of affinities, and the production of new compounds, as when sugar by contact with yeast is resolved into alcohol and carbonic acid.

But in addition to metamorphoses of the kind just alluded to, which, in the various ferments at least, commence spontaneously, air (at all events, at the commencement), moisture, and a certain temperature being the usual conditions, organic substances undergo very well marked decompositions when exposed to the action of heat and of some powerful re-agents; and it seems advisable here to give also a general account of such decompositions, as they admit of being classified under certain heads or rules generally applicable.

We shall here, therefore, briefly describe the changes produced on organic compounds: 1, by oxidation; 2, by the action of acids; 3, by the action of bases; 4, by the action of heat in close vessels, or the destructive distillation; and 5, by the contact of ferments.

Oxidation: a. direct.—The direct oxidation of organic compounds takes two distinct forms. The first is the familiar one of

combustion, in which the action of the atmospheric oxygen is aided by a high temperature. The results differ according to the supply of oxygen. If there be an excess of air, or of oxygen, from any source, the whole of the carbon and hydrogen is converted into carbonic acid and water, which, along with uncombined nitrogen, are the ultimate products of the action of oxygen on organic matters. But if the supply of air be deficient, the hydrogen is oxidized in preference to the carbon, which is deposited as smoke, soot, or lamp-black.

The second form of direct oxidization is that which is commonly called decay, but which Liebig proposes to call *Eremacausis* (*i. e.*, slow combustion), and which takes place when organic matter is exposed to air or moisture. In dry air it does not occur.

One of the most familiar examples of this kind of oxidation is that decay of wood by which it is slowly converted into a dark brown powder—ulmine. In this process, as De Saussure has shown, the wood absorbs oxygen, and produces an equal volume of carbonic acid along with water, and the residue—ulmine. As, in combustion, the oxygen combines by preference with hydrogen, so also in *eremacausis* there is every reason to believe that the absorbed oxygen combines with the hydrogen of the wood, and that an equivalent quantity of oxygen, also derived from the wood, is given off in the form of carbonic acid. Now, since wood may be represented as composed of carbon and the elements of water, and as water and carbonic acid are two of the products of *eremacausis*, it might be supposed that the water was ready formed in the wood, and that the absorbed oxygen had combined with the carbon. But it has been shown that, in presence of hydrogen, carbon does not at the ordinary temperature combine with oxygen, for which its affinity is less powerful; and besides, in the decay of wood, the proportion of carbon in the residue (the ulmine) is constantly greater than in the wood. Thus oak wood, $C_{25}H_{22}O_8$ yield in one stage of decay, ulmine, the composition of which agrees with the formula $C_{25}H_{20}O_{20}$; and in a more advanced stage, an ulmine of the formula $C_{25}H_{18}O_{18}$. Here we see that for every 2 eqs. of hydrogen oxidized by the air, 1 eq. of carbon and 2 eqs. of oxygen have been separated; so that the per centage of carbon in the residue constantly increases, and the final result of *eremacausis* would be a residue of carbon, were it not that, as the proportion of carbon in the ulmine increases, its affinity for the other elements, strengthened by its mass, becomes too powerful to be overcome by the oxygen of the air without the aid of heat. It has been suggested, however, by Liebig, that the process of *eremacausis* may occur under such circumstances as to leave at last a residue of pure carbon. The conditions necessary for this are still unknown; but if we suppose one of these conditions to be a semi-fluid state of the matter undergoing decay, and if we imagine

the process to go on at a very slow rate indeed, the carbon thus eliminated might assume the crystalline form, and thus the diamond might be produced. This is a mere suggestion ; but it has more probability in its favor than any other theory of the production of the diamond.

Other examples of eremacausis are, the acetification of alcohol, and the process of nitrification in which ammonia undergoes eremacausis. These, as well as other instances, will be considered in their proper place.

Eremacausis is greatly promoted by heat and by the presence of alkalies. It is on the contrary, arrested or retarded by cold, dryness, acids, and many salts, such as corrosive sublimate, which has been used to prevent the decay of wood.

There is one circumstance connected with eremacausis, or decay, as above described, which is worthy of special attention. It is, that a substance in a state of eremacausis, if placed in contact with another which is capable of undergoing this change, speedily causes the latter to enter into the same condition of change. This effect of contact may be compared, in one sense, to that of a body in combustion, which sets fire to other bodies ; but in ordinary combustion the high temperature plays an important part, while in eremacausis the effect appears to be due to the communication of motion, from the particles of the decaying body to those of the other substance, which motion, as in the case of fermentation, overturns the existing balance of affinities, unstable as it is in organic compounds, and gives rise to the formation of new products.

The process of eremacausis, or slow oxidation in the atmosphere, is one of very great practical importance, inasmuch as by this means, the elements of dead organic matter are made to assume those forms — namely, the forms of carbonic acid, water, and ammonia — in which they are capable of contributing to the nutrition of new and growing vegetables.

A peculiar species of eremacausis is observed in the case of the simultaneous action of oxygen and ammonia on certain colorless vegetable products, which, absorbing these gases greedily, are thus converted into nitrogenized compounds of very fine blue or purple colors. Of this, we have examples in oricine, erythrine, and phloridzine ; and there is good reason to attribute the formation of indigo, from a juice devoid of blue color, to an action of this kind, since both oxygen and ammonia appear to be necessary to its production. The transformation of alloxantine or of uramile into murexide also depends on the simultaneous action of ammonia and oxygen.

b. Indirect oxidation.—The indirect oxidation of organic compounds may be effected in a variety of ways, as for example, by nitric acid, the action of which we shall presently describe along with that of other acids ; by certain salts, as by permanganate of

potash, which converts sugar, for example into oxalic acid ; or by the employment of a mixture of bichromate of potash and diluted sulphuric acid by which means salicine may be made to yield the hyduret of salicylic acid (oil of spiræa); by the action of sulphuric acid and of peroxide of manganese, as when alcohol is converted into aldehyde ; or finally by the combined action of heat and hydrated alkalies, as when indigo heated with potash gives rise to anthranilic acid, hydrogen being given off ; or acetates, heated with baryta, yield marsh gas and carbonates. The use of fusion with caustic potash as an oxidizing agent is an important means of obtaining a less perfect oxidation than is the result of some of the other processes, and it has lately led to some very interesting discoveries in animal chemistry.

2. *Action of Acids on Organic Compounds.* — This action is very various ; the two acids most frequently employed are the nitric and sulphuric acids, and as might be expected, the former acts more as an oxidizing agent than the latter.

When sugar, for example, is heated with nitric acid, the latter loses oxygen, for nitrous acid is given off in enormous quantity; while the elements of the sugar, by the action of the oxygen are made to combine so as to produce compounds of less complex radicals than that of sugar probably is. Among the products are water, carbonic acid, oxalic acid, and saccharic acid, besides others not yet investigated ; but the three first sufficiently show the tendency of oxidation to promote the formation of less complex radicals.

When nitric acid acts on organic matters, there is generally found one acid, if not more among the products, and in this way a large number of acids have been discovered. Examples of this are, mucic acid from gum ; indigotic and carbazotic acids from indigo ; margaric acid from stearic acid ; suberic and succinic acids, from oily acids, besides many others. It frequently happens that compounds, whether acid or neutral, formed by the action of nitric acid on organic matter, contain hyponitrous acid as a constituent, apparently substituted for some element. This is the case with nitrobenzide from benzine, and with nitronaphthalase, and a whole series of compounds discovered by Laurent in his study of the action of nitric acid on naphthaline. The carbazotic or nitropicric acid also appears to contain a compound of nitrogen and oxygen. Some organic bases, as morphia and brucia, strike a deep red color with nitric acid.

When sulphuric acid is made to act on organic compounds, it chars a considerable proportion of them by virtue of its attraction for oxygen and hydrogen in the form of water. But in many cases it produces very different effects. Thus by boiling with sulphuric acid and water, starch and lignine are converted into grape sugar. In other cases, the sulphuric acid seems to lose so much oxygen as to produce hyposulphuric acid, which enters into combi-

nation with an organic compound, forming a new acid, as when sulphuric acid acts on naphthaline, and form sulphonaphthalic acid ; or on benzoic acid, forming hyposulphobenzoic acid ; or on alcohol under certain circumstances, when an acid is produced containing the elements of hyposulphuric acid and of a carbon-hydrogen. In other cases, the sulphuric acid combines unchanged with the organic compound, as in sulphovinic acid, which is a bisulphate of oxide of ethyle ; sulphomethylic acid, and others.

Many organic compounds, heated with excess of sulphuric acid, are entirely decomposed, yielding water which combines with the acid and other products which are disengaged. Thus oxalic acid is resolved into water, carbonic acid, and carbonic oxide ; formic acid into water and carbonic oxide ; alcohol into water, olefiant gas, and other products.

Several organic compounds are dissolved by sulphuric acid with the production of a fine red or purple color. Salicine strikes a red color with the acid, and cedriret, one of the constituents of tar, dissolves in it with a deep blue color, as does also naphthalase.

Phosphoric acid may be employed in some cases to remove water from organic compounds, as it does not char them. Like sulphuric acid, it forms with oxide of ethyle an acid salt, known as phosphovinic acid.

Hydrochloric acid and its congeners have no very extensive action on organic substances. With alcohol, hydrochloric acid gas yields chloride of ethyle ; and a current of this gas, passed through an alcoholic solution of a fatty acid, gives rise to the compound of the fatty acid with oxide of ethyle, which would otherwise be obtained with difficulty. With oil of turpentine, oil of lemons, and some other essential oils composed of carbon and hydrogen, hydrochloric acid gas combines, forming solids resembling camphor. Pyroxanthine, a substance contained in tar, dissolves in strong hydrochloric acid with a fine and deep purple color.

3. Action of Bases on Organic Compounds.—Hydrated bases unite, of course, with organic acids ; and when heated with neutral substances, they generally give rise to the formation of acids, such as acetic and oxalic acids, or even carbonic acid, oxygen being disengaged, or, (if the organic body contain nitrogen,) hydrogen and ammonia. This property of hydrated bases is employed as a means of converting all the nitrogen of organic compounds into ammonia, and in this form determining its quantity.

The presence of bases greatly promotes the absorption of atmospheric oxygen by organic substances. This is the reason why alkalies assist eremancausis. The same effect is very conspicuous in the change which the salts of gallic acid (and some other acids) undergo when exposed to the air. A solution of an alkaline gallate absorbs oxygen very rapidly, and becomes very dark in color,

being oxidised in a far shorter time than if the acid had been uncombined.

4. *Action of Heat on Organic Compounds in close vessels.* — This action is known under the name of the *destructive distillation*. It must be considered as combustion with a very limited supply of oxygen, that, namely, afforded by the substance itself. A very great variety of compounds is produced, many of them very interesting and useful. The destructive distillation may be considered as it affects substances containing nitrogen, and substances devoid of that element. Many products are common to both cases, but many also are confined to one case, especially to that of nitrogenized substances.

The destructive distillation of non-nitrogenized substances has been chiefly studied in the case of wood, which, when heated in close vessels, yields a great variety of products: some, binary compounds, such as paraffine, naphthaline, eupione, water, carbonic oxide, carbonic acid, marsh gas, and olefiant gas: other ternary, such as acetic acid, $C_4H_2O_3$; hydrated oxide of methyle or pyroxylic spirit, $(C_2H_3)O$, H_2O ; lignone, xylite, mesite, and other volatile etherial liquids, composed of the same elements as pyroxylic spirit, and very similar to it in properties; creosote; picamar; capnomore; cedriret; pittacal, and pyroxanthine, besides many others, not yet properly investigated.

When fatty or resinous bodies are subjected to the destructive distillation, there are obtained, besides other compounds, two solid carbo-hydrogens: chrysene, $C_{22}H_{14}$, and pyrene, $C_{16}H_{10}$; which also occur among the products of the distillation of coal.

This latter distillation may serve as an example, the best known, of the action of heat on nitrogenized organic bodies; for coal contains a certain although small proportion of nitrogen. The products, besides creosote, paraffine, naphthaline, and probably several others of those obtained from wood, include much ammonia, hydrocyanic acid; some peculiar non-nitrogenized acids, as carbolic acid, C_6H_5O , H_2O . (a remarkable compound, having an odour resembling that of creosote, and yielding, when subjected to various re-agents, an extensive series of new compounds [*Runge, Laurent*]); rosolic and humnic acids; and three very remarkable nitrogenized bases, containing no oxygen, namely, kyanol (*aniline, crystalline*), $C_{12}H_7N$ leukol, $C_{10}H_5N$; picoline, $C_{12}H_7N$, (*Anderson*), which is, therefore, isomeric with aniline, besides a fourth not yet fully investigated, pyrrol; finally, paranaphthaline, or anthracene, $C_{20}H_{12}$, and coal tar, naphtha, which is used as a solvent for caoutchouc.

The distillation of animal matter, such as hoofs, horns, or bones, yields analogous results, but is characterized by the very large amount of ammonia which is obtained, animal matter being richer in nitrogen than coal is. This ammonia appears as carbonate,

which salt is thus manufactured, and hence was and occasionally still is, called salt of hartshorn.

Many organic acids, when heated in close vessels to a certain temperature, short of the destructive distillation, undergo a remarkable decomposition; carbonic acid is given off, and there remains a new acid, which is called a pyrogenous acid, or pyro-acid. Thus meconic acid, at a certain temperature, yields carbonic acid and komeonic acid: while komeonic acid, if heated in its turn, yields carbonic acid and pyromeconic acid. We have also pyromucic, pyrotartaric, or pyroracemic and pyrocitric acids; citric acid yielding three pyro-acids, aconitic, (equisetic,) itaconic and citraconic acids, and malic acid also yielding two, maleic and paramaleic or fumaric acids.

From the above statements, it is obvious, that the action of heat on organic compounds gives rise to a very large number of important products of which only the most remarkable have been named. All will be described in their respective places.

5. *Action of Ferments on Organic Compounds.*—Of this action the best known and most important example is the fermentation of sugar, by which it is resolved into alcohol and carbonic acid.

The circumstances under which this metamorphosis occurs are these: the sugar must be dissolved, the solution must have a certain temperature, and there must be present a ferment, such as yeast or some analogous body. In the juice of the grape a ferment, the fibrinous or caseous constituent of the juice is naturally present; and Gay Lussac showed that the contact of atmospheric air was necessary to commence the fermentation, but that this contact with the atmosphere might be only for a very brief period, after which air was no longer necessary. It is obvious that the air acts by inducing a state of change in the ferment, for if any ferment, previously exposed to the air, be added to a pure solution of sugar, fermentation will take place without the mixture being exposed to the air after the ferment has been added.

Berzelius and others conceived that the ferment acts by contact in some way not very clearly defined, by catalysis, as it is called, as they conceive sulphuric acid to do in the formation of ether from alcohol. But Liebig has proved that in this latter case the acid first combines with ether (oxide of ethyle) forming sulphovinic acid (bisulphate of oxide of ethyle), and that this compound at a temperature rather higher than that at which it is formed, is decomposed into hydrated sulphuric acid and ether which distils over. The same chemist has pointed out many other instances of the effect of contact, even in inorganic chemistry: such as the action of oxide of silver on peroxide of hydrogen, where the former compound, by contact with the latter, not only decomposes it, causing oxygen to be rapidly given off, but is itself decomposed, losing all its oxygen; the solution in nitric acid of an alloy of platinum and silver, while platinum alone is insoluble in that acid;

or the action of carbonate of silver on certain organic acids, which cause a disengagement of carbonic acid, this disengagement being attended with a partial reduction of the oxide of silver. These, and many other more familiar cases, particularly those where a compound is decomposed with detonation in consequence of a slight touch, or gentle friction, a moderate elevation of temperature, or the contact of another substance (*e. g.* chloride of nitrogen with oil) all tend, according to Liebig, to establish the doctrine that in certain compounds the balance of affinities is unstable, and therefore easily overturned, either by chemical or by mechanical influences.

The compounds which are capable of fermentation or any similar metamorphosis, are all of them bodies in which such an unstable equilibrium exists: they are all, in point of fact, easily decomposed by many different agencies, such as heat, acids, bases, oxygen, chlorine, &c., &c. Now, we can offer no other explanation of these facts of fermentation than this, that when a body in a state of progressive change, the particles of which are consequently in a state of motion, is placed in contact with another body, the particles of which are in a state of unstable equilibrium, the amount of motion mechanically communicated to the particles of the latter from those of the former, is sufficient to overturn the existing equilibrium, and by the formation of a new compound establish a new equilibrium more stable under the given circumstances.

There is nothing unphilosophical in this explanation, and it is to be considered as the best theory of fermentation yet attempted. According to the view of Liebig, a ferment is merely a compound in a state of decomposition, capable of setting in motion, and thereby bringing also into a state of decomposition, the particles of another compound, the existence of which depends on a nice balance of affinities.

On the other hand the view adopted by Berzelius, according to which fermentation, and all the other phenomena of chemical change produced by contact, are the results of a peculiar unknown force, the catalytic force, coming into action when certain bodies are placed in contact, appears unphilosophical, as, in the first place, assuming the existence of a new force where known forces would suffice to explain the facts; and, secondly, as furnishing no real explanation, but merely acknowledging, indirectly, our inability to offer any such explanation. When we ascribe an effect to catalysis, we are only saying, in other words, that we cannot account for it: catalysis is thus merely a convenient term for all that we do not understand. And to the use of the word in this sense, namely, as a name for the agent which produces certain effects, the agent itself being unknown, there would be no objection, were it not that catalysis has been employed to account for phenomena not only different from each other, but actually of an opposite kind. For example, platinum, in causing the combination of oxygen and

hydrogen, is said to act catalytically, and the action of oxide of manganese, or oxide of silver in decomposing peroxide of hydrogen, that is, in causing the separation of oxygen and hydrogen, is also called catalytic. This example proves how loosely the word has been employed, and how vague are the views which have led to its introduction.

A variety of important and interesting processes come under the head of actions caused by ferments; the production of alcohol from sugar, of oil of bitter almonds from amygdaline, and of lactic and butyric acids from cane of sugar or sugar of milk, are all examples of this; and in each of these cases the ferment is peculiar. In the case of sugar it is yeast, or gluten, undergoing eremacausis and putrefaction; in the case of amygdaline it is emulsine, a peculiar modification of albumen; and in the case of cane sugar or sugar of milk, when converted into lactic or butyric acid, it is caseine, the nitrogenized constituent of the milk.

The access of air is required at first to yield oxygen to the gluten, &c., which then entering into eremacausis, or if air be excluded, into putrefaction, are capable of acting as ferments.

In the actions induced by ferments, we are to distinguish those in which some external element or elements are added to those of the compound, which cases resemble ordinary decompositions, from those in which the elements of the decomposed body merely transpose themselves, producing new compounds. The latter are properly and strictly termed metamorphoses. Fermentations, in which oxygen is absorbed, are examples of eremacausis, and it has already been mentioned that a body in a state of eremacausis acts on other bodies as an excitant of the same change, that is, as a ferment.

Indeed, most ferments, whether they induce eremacausis, or a more pure metamorphosis in other bodies, are themselves in a state of eremacausis, at all events in the commencement of the change.

The subject of fermentation and ferments will be hereafter more especially considered, in connection with fermentescible compounds: here the subject is merely treated in a general way.

Putrefaction, under ordinary circumstances, partakes largely of eremacausis, and differs from the ordinary kind only in the offensive odor of some of the products, chiefly compounds of sulphur and phosphorus, as sulphuretted and phosphuretted hydrogen.

When air is excluded, putrefaction goes on, provided moisture be present, and it is then a metamorphosis, giving rise, in the case of vegetable matter putrefying under water, or in the strata of mines, to gaseous products, such as marsh gas and olefiant gas, constituting with air the fire-damp, and carbonic acid, which is the choke-damp of the miner.

Animal matter, in a state of putrefaction, as putrid flesh, blood, cheese, or wine, acts as a ferment, and is capable of causing the metamorphosis of sugar into alcohol and carbonic acid, as well as of inducing eremacausis, and also propagating a putrefactive decomposition analogous to its own. Thus, it is well known that fresh cheese, if inoculated with decaying cheese, soon passes into decay, spreading from the seat of the inoculation.

We shall, hereafter, see that it is probable that some poisons and miasmata act as ferments on the blood. The singular sausage poison of Wurtemberg is animal matter in a peculiar state of decay, and does not contain any poisonous *compound*, only a poisonous *state* or *condition*; and the same principle may hereafter be found to furnish the true explanation of contagions.

Fermentation, putrefaction, and eremacausis, are all promoted by the same circumstances, and arrested by the same influences. Antiseptics are substances, which, by combining with the ferment, or a part of it, or even with the body to be fermented, prevent the continuance either of the decomposition in the ferment, or of the fermentation itself. Corrosive sublimate and arsenic, which are powerful antiseptics, combine with animal matter, and form with it stable compounds; creosote combines energetically with albumen, &c.

In fermentation, properly so-called, the elements of the ferment take no chemical share in the metamorphosis of the body acted on by the mechanical agency above explained. That body is resolved into two or more new compounds of less complex radicals. The elements of water may or may not take part in the change; when they do, as in the case of sugar, the weight of the products, in this case alcohol and carbonic acid, is equal to that of the sugar, *plus* a certain weight of water. As, when the water is passed in vapor over carbon at a white heat, the carbon is shared between the oxygen and hydrogen, producing carbonic acid (or oxide), and carburetted hydrogen, so in the metamorphosis of sugar, and other analogous cases, we have on the one hand an oxidized compound, (in the case of sugar represented by carbonic acid), and on the other a compound in which part of the carbon is united to all the hydrogen (in the case of sugar, the alcohol). Similar results are obtained when alcohol or acetic acid are metamorphosed by heat, and this may be viewed as a general character of the metamorphosis of non-nitrogenized bodies; namely, that the carbon is divided between the oxygen and hydrogen.

In putrefaction, again, the ferment plays a chemical part in the change, and two or more compounds, the ferment and the putrefying body or bodies, combine to give rise to new compounds, with or without the elements of water. Putrefaction is generally the characteristic transformation of nitrogenized compounds, and the very great tendency of such compounds to undergo transformations is well illustrated by the spontaneous metamorphosis of a

solution of cyanogen in water. Such a solution contains the four principal elements of organic bodies; and its transformations may be said to be the only case of putrefaction which has been as yet carefully studied.

The solution after a time becomes brown and turbid, and deposits a dark matter, containing ammonia, united to a compound formed of the elements of cyanogen along with those of water. This matter being insoluble, undergoes no further change. Such a compound might arise from the re-action between 2 eq. cyanogen, and 4 eq. water: thus $2 \text{C}_2 \text{N} + 4 \text{H}_2 \text{O} = \text{NH}_3 + (\text{C}_4 \text{H}_2 \text{N}_2 \text{O}_4)$; according to some, the brown matter contains no ammonia, and is $\text{C}_4 \text{N}_2 \text{H}_2 \text{O} = 2 \text{C}_2 \text{N} + \text{H}_2 \text{O}$.

Another change is that in which water is decomposed, each of its elements uniting with cyanogen, and producing cyanic and hydrocyanic acids: thus, $2 \text{H}_2 \text{O} + 2 \text{C}_2 \text{N} = (\text{C}_2 \text{N}_2 \text{O} + \text{H}_2 \text{O}) + \text{H}_2 \text{C}_2 \text{N}$.

Another metamorphosis gives rise to oxalic acid and ammonia. In this case, 1 eq. cyanogen acts on 3 eq. water: thus, $\text{C}_2 \text{N} + 3 \text{H}_2 \text{O} = \text{NH}_3 + \text{C}_2 \text{O}_3$.

But cyanic acid cannot exist in contact with water and other acids: it is instantly metamorphosed into bicarbonate of ammonia thus, $\text{C}_2 \text{N}_2 \text{O} + 3 \text{H}_2 \text{O} = \text{NH}_3 + 2 \text{CO}_2$.

Toward the end of the process, when ammonia has become predominant, the cyanic acid produced undergoes a different metamorphosis. It now unites with water and ammonia, and may possibly for a time exist as hydrated cyanate of ammonia; but at all events that salt, if formed at all, is soon transformed into urea: $\text{NH}_3 + \text{C}_2 \text{N}_2 \text{O} + \text{H}_2 \text{O} = \text{C}_2 \text{H}_4 \text{N}_2 \text{O}_2 = \text{urea}$.

Again, the hydrocyanic acid gives rise to another brown solid body, containing cyanogen or paracyanogen (possibly mellone also), and hydrogen; and, along with this, oxalic acid, urea, and carbonic acid, by metamorphoses already described.

Lastly, the hydrocyanic acid in contact with water, and an acid or an alkali (here oxalic acid or ammonia), undergoes another metamorphosis, and is transformed into formic acid and ammonia: thus, $\text{H}_2 \text{C}_2 \text{N} + 4 \text{H}_2 \text{O} = \text{NH}_3 + \text{C}_2 \text{H}_2 \text{O}_3, \text{H}_2 \text{O}$.

Thus cyanogen, a binary compound, along with water, another binary compound, gives rise to no less than eight different compounds: 1st, the black compound, containing the elements of cyanogen and those of water, possibly $\text{C}_4 \text{H}_2 \text{N}_2 \text{O}$; 2d, ammonia, NH_3 ; 3d, cyanic acid, $\text{H}_2 \text{O C}_2 \text{N}_2 \text{O}$; 4th, hydrocyanic acid, $\text{H}_2 \text{C}_2 \text{N}$; 5th, oxalic acid, $\text{C}_2 \text{O}_3$; 6th, carbonic acid; 7th, a brown solid, containing cyanogen (paracyanogen) and hydrogen; 8th, formic acid, $\text{C}_2 \text{H}_2 \text{O}_3, \text{H}_2 \text{O}$; and in addition to these, three bodies, formed by the combination of two of the above eight, and containing all the four elements; namely, 9th, oxalate of ammonia; 10th, bicarbonate of ammonia; 11th, urea.

This striking example is well adapted to give a clear idea of the immense variety attainable, when, instead of two binary compounds, two ternary or two quaternary compounds, along with water, are concerned; and of the slight modifications of external circumstances which are required to produce results so varied, all the above substances being produced in a liquid at the usual temperature.

It is hoped that the above sketch of the doctrine of the chemical changes and metamorphoses of organic compounds will suffice to enable the student to follow the individual processes and reactions, to be hereafter mentioned, which owing to our limited space, we must treat with great brevity. We shall now conclude our introductory matter by some general observations on the doctrines now held by many chemists on the subject of the organic acids; after which we shall enter on the study of the known original radicals.

ORGANIC ACIDS.

The acids met with in organic chemistry are principally compounds of carbon, hydrogen, and oxygen, although some do contain also nitrogen. They are distinguished from inorganic acids by their high atomic weight, and by the action of heat, which decomposes them all. As, in many of them, the oxygen they contain is a multiple by a whole number of the oxygen of the bases which neutralize them, so they are viewed as oxygen acids by those who consider true sulphuric acid to be an oxygen acid, SO_3 , and oil of vitriol to be its hydrate, $\text{H}_2\text{O}, \text{SO}_3$. In the case of acetic acid, for example, the formula of which is $(\text{C}_4\text{H}_3)\text{O}_3\text{H}$, the compound $(\text{C}_4\text{H}_3)\text{O}_3$, unknown in a separate form is called dry acetic acid, and the strong acetic acid is considered as its hydrate; and the analogy is supposed to be fortified by the fact that dry acetic acid, like dry sulphuric acid, contains 3 eq. oxygen, and neutralizes 1 eq. of base, MO , containing 1 eq. of oxygen.

But a careful study of the organic acids leads us to apply to them the same theory which we have already adopted for the inorganic acids, and to consider them as compounds of hydrogen, with compound radicals, usually consisting of carbon, hydrogen, and oxygen. On this view, as oil of vitriol is H_2SO_4 , the strongest acetic acid is $\text{H}_2(\text{C}_4\text{H}_3)\text{O}_4$. It is true that this radical, $(\text{C}_4\text{H}_3)\text{O}_4$, does not exist, or is not known in the separate form; but the same remark applies to dry acetic acid, $(\text{C}_4\text{H}_3)\text{O}_3$, which on the old view is supposed to be combined with water, for it also is unknown in the separate state.

The existence of compound radicals in organic acids is not more difficult to imagine than that of SO_4 , the compound radical of sulphuric acid, for $(\text{C}_4\text{H}_3)\text{O}_4$, only differs from it in containing three elements instead of two; indeed, as some ternary organic radicals are known in the separate form, we actually derive an argument

from organic acids in favor of the existence of compound radicals in inorganic acids. Thus, the radical or organic metal, cacodyle, forms cacodylic acid.

But we find, among organic acids, a much larger proportion which are bibasic, tribasic, in short, polybasic, than occurs among inorganic acids. Referring to what was said of the monobasic, bibasic, and tribasic phosphoric acids, it will be easily understood, that while acetic acid, for example, is monobasic, tartaric acid, malic acid, konic acid, alloxanic acid, and others are bibasic; that citric acid and meconic acid are tribasic, and that saccharic acid is quinquebasic. And as the three modifications of phosphoric acid were described on the old view as monohydrated, bihydrated, and terhydrated, and on the new view, as containing respectively, 1, 2, and 3 eqs. of hydrogen, replaceable by metals, so tartaric acid may be either $C_4H_4O_{10}$, $2H_2O$, or $C_4H_4O_{12}H_2$; malic acid may be $C_4H_4O_8$, $2H_2O$, or $C_4H_4O_{10}H_2$; and so on; while citric acid may be either $C_6H_5O_{11}$, $3H_2O$, or $C_6H_5O_{14}H_3$, and meconic acid, $C_{14}H_9O_{11}$, $3H_2O$, or $C_{14}H_9O_{14}H_3$; and lastly, saccharic acid may be $C_{12}H_{11}O_{11}$, $5H_2O$; or $C_{12}H_{11}O_{16}H_5$.

In such polybasic acids, there is always some hydrogen in the radical, of which it is a constituent, and some combined with the radical, and replaceable by its equivalent of metals. It is only this latter hydrogen, the amount of which affects the neutralizing power of the acid.

Now, among the phenomena of the action of bases on organic acids, we have some facts which seem almost to demonstrate the existence of this replaceable hydrogen, as such, and thus to establish the new theory of acids. Thus, meconic acid, which is tribasic, forms, like tribasic phosphoric acid, three series of salts, in which 1, 2, or 3 eq. of hydrogen, are replaced by metal. But while the meconic acid, as well as the tribasic phosphoric acid, readily forms with oxide of the silver, the salt in which all the hydrogen is replaced by silver; it cannot form, or forms with difficulty, a similar salt with potash, with which it forms, very easily, salts, with 1 and 2 eqs. of metal, and 2 or 1 eqs. of hydrogen.

Here we have the apparent contradiction of a weak base, oxide of silver, neutralizing the acid easily and completely; while a strong base, potash, leaves it imperfectly neutralized. This cannot, I think, be accounted for on the old view, and many similar cases might be mentioned. On the new view, such apparent anomalies disappear: for since the neutralizing depends on the replacement of hydrogen by a metal, it is evident that an oxide which is easily reduced, or deprived of its oxygen by hydrogen, like oxide of silver, will most easily neutralize acid, while a difficultly reducible oxide, such as potash, cannot be so far reduced as to yield 3 eq. of metal, so as to form the neutral salt.

There are other kinds of organic acids which are what may be called coupled acids; that is to say they contain an acid coupled with another body, which does not neutralize the acid, but accompanies it in all its combinations. Thus, in hyposulphonaphthalic acid, $C_{10}H_8S_2O_5$, H_2O , we have hyposulphuric acid, S_2O_3 , coupled with naphthaline, $C_{10}H_8$, and the coupled acid neutralizes exactly as much base as the hyposulphuric acid alone would do. Again, formobenzoic acid, $C_8H_7O_3$, H_2O , may be viewed as a coupled acid, consisting of formic acid O_2H , O_2 , H_2O , and oil of bitter almonds (hyduret of benzoyle) $C_7H_5O_2$, which neutralizes just as much base as the formic acid alone. Those coupled acids which contain hyposulphuric acid, as is often the case, are formed by the action of oil of vitriol, or of anhydrous sulphuric acid, on organic bodies, when 2 eq. of acid, losing 1 eq. of oxygen, form hyposulphuric acid; which commonly unites with the organic matter *minus* 1 eq. hydrogen, that hydrogen having combined with the oxygen derived from the sulphuric acid.

IN the following pages we shall adopt the arrangement of Liebig, which has the advantage of uniting those substances which are naturally allied in composition. It proceeds, in the first place, on the principle of describing, under each known or admitted organic radical, all the compounds derived from or closely connected with it. After having gone through these, it takes up the consideration of the best known organic acids, including the oily acids; then the neutral oils, fat, and essential; the resins; the non-nitrogenous coloring matters, bitter and extractive principles, nitrogenized coloring matters, and their congeners; the organic bases; starch; gum; woody fibre; destructive distillation of wood, of lignite, of coal; nitrogenized and sulphurized vegetable principles, albumen, &c., the modifications of these in the animal kingdom; bile; nervous matter; gastric juice; saliva; excrements; urine; blood; lymph, &c. And the whole is wound up with considerations on the nutrition of plants and animals.

This arrangement is not a scientific one, and in the present state of our knowledge such an arrangement is, I fear, unattainable. But it is very convenient, and, by judicious grouping, very much facilitates the learning and the retaining in the memory of the immense mass of facts which at present constitute organic chemistry.

We proceed, therefore, to consider those organic radicals which are admitted by the best authorities, although they are not always known in the separate state. The first compound radicals that attract our attention are certain binary ones, already mentioned as binary compounds, but not in their character of radicals, in the first part of this work; these are amide or amidogen, cyanogen, and carbonic oxide.

I. AMIDE. $NH_2 = Ad = 16.19$.

Syn. Amidogen. — It has already been mentioned that certain compounds exist, in which we can hardly doubt that this substance is present. Thus, potassium or sodium, heated in dry ammoniacal gas, disengages 1 eq. of hydrogen, forming the compound KNH_2 or $NaNH_2$. When these are put into water, potash or soda is formed, while ammonia is set free: $K, NH_2 + H_2O = KO + NH_3$. Again, when oxalate of ammonia, NH_3, HO, C_2O_3 is heated, there are formed, water which distils over, and the compound $NH_2 C_2 O_3$ which remains behind: thus, $NH_3, HO, C_2 O_3, O_2 = 2 H_2 O + NH_2 C_2 O_3$. The latter compound is called oxamide, and is a sparingly soluble white powder, neutral or indifferent in itself, but yielding, when digested with an alkali, ammonia, which escapes, and oxalic acid, which combines with the alkali. Or if oxamide be heated with diluted sulphuric acid, it yields ammonia which combines with the acid, and oxalic acid which crystallizes in cooling. In both cases, water is decomposed: thus, $NH_2 C_2 O_3 + 2 H_2 O = NH_3, HO + C_2 O_3$.

Now oxamide is interesting, as being the type of a class of compounds, all of which, when heated with an alkali or an acid, yield ammonia and an acid, the ammonia and the anhydrous acid together containing just 1 or 2 eqs. of water more than the compound which, with the aid of water, has yielded them. If we consider oxamide as $NH_2 + C_2 O_3$; that is, as composed of amide (or ammonia *minus* hydrogen NH_2), and the radical carbonic oxide (or oxalic acid *minus* oxygen $C_2 O_3$), then all its congeners are likewise compounds of amide, on the one hand, and an anhydrous organic acid, *minus* oxygen, on the other. On this view benzamide is benzoate of ammonia, *minus* water, $(NH_3 + C_6 H_5 O_2, HO) - 2 H_2 O = NH_3 + C_6 H_5 O_2$; or it is amide *plus* benzoyle (the radical of benzoic acid, $(C_6 H_5 O_2)$). Therefore, when benzamide is acted on by potash, ammonia is given off, and benzoate of potash is left; and when it is heated with an acid, a salt of that acid with ammonia is obtained, while benzoic acid crystallizes. There are a good many similar compounds which are called amides, and are viewed as compounds of amide.

It is obvious that the distinctive characters of amide, which is not known in the separate form, are its powerful affinity for hydrogen, and its equally strong tendency to combine with radicals which have a very great affinity for oxygen, such as those already mentioned, potassium, sodium, the radical $C_2 O_3$, and the radical benzoyle. It is probably, on account of its having so great an affinity for elements of the most opposite kind, that we cannot obtain it in the separate form.

With hydrogen amide forms two compounds, ammonia, $Ad H$, and ammonium, $Ad H_2$. The former may be called, in this view,

hydramide. The latter (as has been already explained at p. 88) is considered to be a compound metal.

It is very remarkable, that when ammonia or hydramide combines with an acid, the resulting compound is not a salt, unless the acid contain hydrogen. Thus, hydramide, with dry sulphuric acid, SO_3 , forms a compound which is not sulphate of ammonia, and is not a salt at all. But if, instead of SO_3 , we employ oil of vitriol, H_2O , SO_3 , or H_2SO_4 , sulphate of ammonia, a true salt, is obtained.

Here we may conclude that Ad H , in contact with H_2SO_4 , takes the hydrogen, forming ammonium, and that the resulting salt is composed of $\text{Ad H}_2 + \text{SO}_4$; that is, a metal combined with the sulphuric acid radical, just as sulphate of potash is K_2SO_4 . In all true salts of ammonia, therefore, $\text{Ad H}_2 = \text{Am}$ (ammonium) occupies the place of a metal, and may be replaced by a metal; and even if we consider sulphate of potash to be K_2O , SO_3 , we have only to view the sulphate of ammonia as NH_4O , $\text{SO}_3 = \text{Ad H}_2\text{O}$, $\text{SO}_3 = \text{AmO}$, SO_3 , that is, sulphate of oxide of ammonium.

It must be borne in mind, however, that although all the chemical relations of these compounds confirm the ammonium theory, yet neither ammonium nor its oxide are capable of existing uncombined; for ammonium, when separated, is resolved into ammonia and hydrogen; and oxide of ammonium, when separated, assumes the forms of ammonia and water.

Of the chief compounds of amide, ammonia or hydramide has been previously described. It remains for us to direct attention to this substance as constantly present in the atmosphere in minute quantity, from whence it descends in the rain, being an absolutely indispensable agent in vegetation. We have already seen that the putrefaction and eremaucausis of nitrogenized compounds yields carbonate of ammonia as a product. Its presence in the air is therefore certain, *a priori*, even although we cannot detect it until it is condensed and accumulated in rain. It is, however, absorbed from the air by almost all minerals and soils, especially aluminous and ferruginous soils: hence a trace of ammonia is often found where it is not expected, and where it has been erroneously believed to have been formed by the direct union of hydrogen and nitrogen.

This is the true explanation of the very remarkable and accurate experiments of Faraday, which have lately been confirmed by Will and Varrentrapp.

As an ingredient of manures, ammonia is most valuable. Its action on growing vegetables will be hereafter explained.

Ammonia forms a large number of compounds with the oxides of metals, the chlorides of metals, of sulphur, and of phosphorus, and finally with salts in general. These belong rather to inorganic

chemistry, and the limited size of this work forbids us to describe them in detail.

But it is proper here briefly to notice the compounds formed by amide with metals, inasmuch as amide is here viewed as an organic radical, and some of these compounds are very important in reference to organic chemistry.

Amide then forms compounds with potassium, sodium, mercury, copper, silver, and platinum. The two former are of a greenish olive color, and their action on water has been described above. The amide or amidide of mercury, Hg Ad, is not known in a separate state, but forms with bichloride of mercury the salt called white precipitate, $\text{Hg Ad} + \text{Hg Cl}_2$.

This salt is prepared by adding ammonia to a solution of bichloride of mercury. When boiled with potash, it yields another salt, $\text{Hg Ad} + \text{Hg Cl}_2 + \text{Hg O}_2$. The amidide of mercury also combines with the basic sulphate, and the basic nitrates of the same metal, forming with the basic protonitrate, the soluble mercury of Hahnemann.

The amidide of copper, Ad, Cu, is only known in combination with the hyposulphate and with the nitrate of ammonia.

The amidide of silver, Ag Ad, is known in combination with the nitrate, sulphate, seleniate and chromate of ammonia.

But it is the amidide of platinum which offers the greatest interest, as it gives rise to several very singular compounds, exhibiting the characters of very powerful bases. These remarkable substances have been studied by Gros, Reiset, and very recently by Peyrone, but are yet far from being understood. We shall endeavor briefly to state what is known of them.

When bichloride of platinum, Pt Cl_2 , is heated for some time to nearly the melting point of tin, it loses half its chlorine, and is converted into protochloride, Pt Cl , which forms a powder of a dirty brownish green color, insoluble in water. By continued digestion in ammonia, with the aid of heat, the protochloride is first changed into a green crystalline compound, which finally dissolves entirely, forming a yellowish solution, which on evaporation deposits yellowish white prismatic crystals. The green crystalline compound, discovered by Magnus, contains the elements of protochloride of platinum and those of ammonia, Pt Cl NH_3 ; the yellowish white crystals, discovered by Reiset, contain twice as much ammonia and the elements of water, $\text{Pt Cl}, 2 \text{ NH}_3 + \text{aq}$.

These two compounds are very remarkable: neither of them contains ammonia as such; both are insoluble in hydrochloric and dilute sulphuric acids. But the green compound of Magnus dissolves in nitric acid, with evolution of nitrous acid, and the solution, on cooling, deposits white crystalline scales, while the liquid contains no ammonia. These white scales, discovered by Gros, are the nitrate of a new base, $\text{Pt Cl N}_2 \text{ H}_2 \text{ O}$; which may be derived

from 2 eq. of the insoluble compound of Magnus, $\text{Pt}_2 \text{Cl}_2 \text{N}_2 \text{H}_6$, by the loss of 1 eq. of protochloride of platinum, and the addition of 1 eq. of oxygen. This base acts exactly like the basic oxide of a metal, or like oxide of ammonium, $\text{N H}_4 \text{O}$, combining with acids and forming neutral salts. It not only forms salts with nitric and sulphuric acids and the like, but with hydrochloric acid it yields a heavy crystalline powder, which is a chloride, bearing the same relation to the base as chloride of ammonium, $\text{N H}_4 \text{Cl}$ (sal ammoniac), does to oxide of ammonium. This chloride, therefore, is $\text{Pt Cl N}_2 \text{H}_6 \text{Cl}$, and the radical of the oxide or base and of the chloride, will be $\text{Pt Cl N}_2 \text{H}_6$, corresponding to ammonium, N H_4 . Although Gros did not isolate either the radical or its oxide, yet from the characters and composition of its salts there can be no doubt of its existence. If we represent this radical, $\text{Pt Cl N}_2 \text{H}_6$ by R , then we have

R O = oxide, the base of the salts, analogous to K O or N H_4

$\text{R O} + \text{S O}_3 = \text{R} + \text{S O}_4$ = sulphate, analogous to K, S O_4

$\text{R O} + \text{N O}_3 = \text{R} + \text{N O}_6$ = nitrate; analogous to K, N O_6

R Cl = chloride, analogous to K Cl or $\text{N H}_4 \text{Cl}$.

The soluble crystalline compound of Reiset, $\text{Pt Cl N}_2 \text{H}_6 + \text{aq.}$, when heated to 212° , becomes anhydrous, and is then $\text{Pt Cl N}_2 \text{H}_6$, that is, it has the same composition as the radical of the base and salts of Gros. But it is not this radical; on the contrary, it is the chloride of a different radical, $\text{Pt N}_2 \text{H}_6$, and its true formula is $\text{Pt N}_2 \text{H}_6 + \text{Cl}$.

This new radical is also perfectly analogous to ammonium, as may be exhibited in a tabular form as follows.

	Chlorine Comp'nd.	Sulphate.	Nitrate.	Double Chloride. with Platinum.
Ammonium $\text{N H}_4 = \text{Am}$	Am Cl	Am S O_4	Am N O_6	$\text{Am Cl} + \text{Pt Cl}_2$
Radical of Reiset } $\text{Pt N}_2 \text{H}_6 = \text{R}'$	$\text{R}' \text{Cl}$	$\text{R}' \text{S O}_4$	$\text{R}' \text{N O}_6$	$\text{R}' \text{Cl} + \text{Pt Cl}_2$

In the case of ammonium, we cannot isolate the oxide $\text{Am O} = \text{N H}_4 \text{O}$, as it instantly resolves itself into ammonia and water, $\text{N H}_3 + \text{H}_2 \text{O}$. But the oxide of Reiset's platinum radical, $\text{R}' \text{O} = \text{Pt N}_2 \text{H}_6 \text{O}$, or rather its hydrate $\text{Pt N}_2 \text{H}_6 \text{O} + \text{aq.}$, is easily obtained from the sulphate by adding just so much baryta as will remove the sulphuric acid, and evaporating the filtered solution in vacuo, when the hydrated oxide crystallizes in colorless needles. This compound is strikingly analogous to hydrate of potash: it is a powerful caustic, attracts carbonic acid from the air as strongly as potash, and exhibits all the chemical characters of one of the strongest alkalies. Few compounds are so remarkable as this base. We shall call it the base α .

This singular compound may be viewed as containing the elements of protoxide of platinum, ammonia and water, Pt O, 2 N

H_2 , H_2O . When heated to 212° , it loses its water and half its ammonia, leaving a compound $PtNH_3O$, or PtO, NH_3 , which appears to be another new base b , combining with acids and forming salts which detonate when heated. This last compound, when heated in the air, burns like tinder, and leaves metallic platinum. It is the oxide of a third radical, b , $= PtNH_3$.

With hydrochloric acid, the base a of Reiset yields water, and the original chlorine compound: thus, $PtN_2H_6, O + HCl = PtN_2H_6, Cl + H_2O$. When this chloride is heated to from 265° to 290° , it loses ammonia and there is left a yellow powder, discovered by Peyrone, which dissolves easily in hot water, and has the composition of the green insoluble crystalline compound of Magnus, $PtClNH_3$, of which it is an isomeric modification. Indeed, the compound of Magnus, (although insoluble in hot water), if boiled with a saturated solution of sulphate or nitrate of ammonia, dissolves, and is deposited, on cooling, in yellow crystals. The yellow ammoniated protochloride of platinum of Peyrone readily dissolves in ammonia, and the solution yields fine colorless prisms of the original chlorine compound of Reiset, but apparently not containing 1 eq. of water of crystallization, which is said to be present in the yellowish-white crystals obtained by Reiset from the green compound of Magnus.

When the yellow compound of Peyrone is acted on by nitrate of silver, it yields chloride of silver, and two new compounds containing nitric acid and platinum, one of which forms yellow octahedrons.

If the sulphate of Reiset's base, $PtN_2H_6 + SO_4$, be acted on by iodide of barium, BaI , there is formed sulphate of baryta, $BaSO_4$, and a protoiodide of Reiset's radical, a , PtN_2H_6, I . This iodide is soluble and crystallizable, and when boiled with water loses ammonia, while a new iodine compound is precipitated, $PtNH_3, I$, corresponding to the chlorine compound of Peyrone and to that of Magnus, both of which are $PtNH_3Cl$.

This new iodine compound seems to be the iodide of the third radical, b , $PtNH_3$; for when acted on by nitrate or sulphate of silver, it yields iodide of silver, and a nitrate or sulphate of this new radical or of its oxide, $PtNH_3, I + Ag, SO_4 = PtNH_3, SO_4 + AgI$; and $PtNH_3, I + Ag, NO_3 = PtNH_3, NO_3 + AgI$. These new salts may of course be represented as $PtNH_3, O + SO_3$, and $PtNH_3, O + NO_2$. With ammonia, these salts yield the nitrate and sulphate of Reiset's base, a ; and with hydrochloric acid they yield the yellow compound of Peyrone. This would indicate that the latter compound is $PtNH_3, Cl$, the chloride of the radical $PtNH_3$, while the green salt of Magnus may be the ammoniated protochloride of platinum $PtCl + NH_3$, or probably $PtCl, NH_3 + aq$.

Here we have at all events, three very remarkable compounds, which contain platinum and the elements of ammonia. There is,

first, the radical *b* last described, Pt N H_3 ; secondly, the radical of Reiset's base, *a*, $\text{Pt N}_2 \text{ H}_6$; and thirdly, the radical of Gros's base, $\text{Pt Cl N}_2 \text{ H}_6$.

Now we have given the history of these compounds somewhat minutely, because their existence throws much light on the nature of a numerous and important class of bodies, namely, the vegetable bases or alcaloids.

It will be observed, then, that the three new radicals above described all contain nitrogen; indeed, all contain the elements of ammonia, and are in their chemical relations entirely analogous to ammonium. Thus we have

	Radical.	Oxide.	Chloride.	Sulphate.
Ammonium.	N H_4	$\text{N H}_4 + \text{O}$	$\text{N H}_4 + \text{Cl}$	$\text{N H}_4 + \text{SO}_4$
Radical of Reiset's base <i>b</i> .	Pt N H_3	$\text{Pt N H}_3 + \text{O}$	$\text{Pt N H}_3 + \text{Cl}$	$\text{Pt N H}_3 + \text{SO}_4$
Radical of Reiset's base <i>a</i> .	$\text{Pt N}_2 \text{ H}_6$	$\text{Pt N}_2 \text{ H}_6 + \text{O}$	$\text{Pt N}_2 \text{ H}_6 + \text{Cl}$	$\text{Pt N}_2 \text{ H}_6 + \text{SO}_4$
Radical of Gros's base.	$\text{Pt Cl N}_2 \text{ H}_6$	$\text{Pt Cl N}_2 \text{ H}_6 + \text{O}$	$\text{Pt Cl N}_2 \text{ H}_6 + \text{Cl}$	$\text{Pt Cl N}_2 \text{ H}_6 + \text{SO}_4$

That the above formulæ represent in some respects truly the relation of these new bases to one another is rendered probable by the fact that, while the radical and base *b* of Reiset differ from his radical and base *a*, by containing 1 eq. of ammonia less, and these last from those of Gros by containing 1 eq. of chlorine less, we can actually transform the salts of Reiset's base *b* into those of his base *a*, by the addition of ammonia; and the nitrate of Reiset's base *a*, by the addition of chlorine, yields a salt having the properties of the nitrate of Gros's base.

Now we have seen that ammonium may be viewed as a compound of amide, as $\text{N H}_2 + \text{H}_2 = \text{Ad H}_2$. May we not, therefore, suppose the new radicals to be also compounds of amide? May not Reiset's radical *b* be ammonium, in which 1 eq. of hydrogen has been replaced by 1 eq. of platinum, $\text{Ad } \begin{Bmatrix} \text{H} \\ \text{Pt} \end{Bmatrix}$? Again, just as we have seen in acids, viewed as hydrogen compounds, analogous elements added to the radical without affecting the neutralizing power of the acid, which remains the same as long as the *replaceable* hydrogen continues unchanged, we can suppose amide to be a basic radical, forming with hydrogen the base ammonia, but capable of taking up into the radical analogous elements without affecting the basic character of the ammonia, because we have now the hydrogen compound of an analogous, but more complex basic radical. On this view, Reiset's radical *b*, may be the hydro-

gen compound of a basic radical more complex than amide; in fact, amidide of platinum. Its formula would then be $\text{Ad Pt} + \text{H}$; and although on this view it should correspond to ammonia, rather than ammonium, we cannot speak positively, as this is the least known of the three.

The other two radicals may be readily viewed as hydrogen compounds of complex amidides, as ammonium is the hydrogen compound of amidide of hydrogen.

Amide, $\text{NH}_2 = \text{Ad}$, with hydrogen forms ammonia Ad H , and ammonium $\text{Ad H} + \text{H}$. In like manner in the radical α of Reiset's salts, we have a complex amide, composed of amide and amidide of platinum, $\text{Ad} + \text{Pt Ad} = \text{Pt Ad}_2$, which, with 1 eq. of hydrogen, may be supposed to form a compound analogous to ammonia, $\text{Pt Ad}_2, \text{H}$, and with 2 eq. of hydrogen actually does form the radical α of Reiset, $\text{Pt Ad}_2 \text{H} + \text{H}$, exactly analogous to ammonium. So the radical of Gros may be derived from the complex amide $\text{Pt Cl Ad} + \text{Ad} = \text{Pt Cl Ad}_2$, which may form $\text{Pt Cl Ad}_2 + \text{H}$ and $\text{Pt Cl Ad}_2 \text{H} + \text{H}$, the latter being the actual composition of the radical of Gros, corresponding to ammonium.

It may also be mentioned, that just as we may view ammoniacal salts as containing ammonia and water rather than ammonium and oxygen, so the base b of Reiset may be $\text{NH}_3 + \text{Pt O}$, analogous to $\text{NH}_3 + \text{H O}$ in the salts of ammonia. If sulphate of ammonia be $\text{NH}_3, \text{H O} + \text{SO}_3$, the sulphate of Reiset's base b will then be $\text{NH}_3, \text{Pt O} + \text{SO}_3$, the protoxide of platinum here playing the part of water, or in other words, platinum playing the part of hydrogen, a substitution far from unnatural or improbable. Again, if we consider the ammoniacosulphate of copper to be

$$\left. \begin{array}{l} 2 \text{NH}_3 \\ \text{Cu O} \end{array} \right\} + \text{SO}_3, \text{ then the sulphate of Reiset's base } a \text{ will be}$$

$$\left. \begin{array}{l} 2 \text{NH}_3 \\ \text{Pt O} \end{array} \right\} + \text{SO}_3, \text{ where platinum replaces copper, also a not}$$

improbable substitution. Reiset is disposed to adopt this view.

The chloride of Gros's radical, $\text{Pt Cl N}_2 \text{H}_2 + \text{Cl}$, may be viewed as a compound of bichloride of platinum with ammonia, $\text{Pt Cl} + 2 \text{NH}_3$, and there is even reason to think that compounds of that radical may be obtained from the solution of bichloride of platinum in ammonia.

From the above remarks it will appear that every probable view which can be taken of these very interesting bases connects them with amide, ammonia, or ammonium, and it is for this reason that they have been treated of in this section. Many pages might be filled with details concerning them; but we have here only indicated those points which will help to elucidate the constitution of the vegetable alkalies.

That important class of compounds not only contains nitrogen, as an essential element, but exhibits the same analogy with am-

monia which we have seen to exist in the compound platinum bases. Moreover, like these bases, the alcaloids do not appear to contain ammonia *as such*; and the probability is very great that their constitution is analogous to that of the bases now described. Recent researches by Berzelius, not yet published, are said to have established that the organic bases contain ammonia, coupled with other compounds.

II. CARBONIC OXIDE (as a Radical). $C_2 O_2 = 28.106$.

SYN. Oxalyle.—There is good reason to believe that the radical of oxalic acid is formed of 2 eq. of carbonic oxide. It has long been known that carbonic oxide, in the sun's light, combines with chlorine to form phosgene gas or chlorocarbonic acid, CO , Cl , or $C_2 O_2$, Cl_2 . This compound may be viewed as the chloride of the radical $C_2 O_2$, or as carbonic acid in which 1 eq. of oxygen is replaced by chlorine, $C \begin{Bmatrix} O \\ Cl \end{Bmatrix}$, corresponding to $C \begin{Bmatrix} O \\ O \end{Bmatrix}$ or CO_2 . But the existence of this radical is more securely inferred from the combinations it forms with oxygen, potassium, and amide.

CARBONIC OXIDE AND OXYGEN.

1. OXALIC ACID. $(C_2 O_2) O + H O$, or $C_2 O_4$, $H = 44.132$.

This acid occurs in nature, generally in the form of an acid oxalate of potash in certain vegetable juices, such as that of oxalis acetosella, also as oxalate of lime in many lichens. It is formed artificially by the action of nitric acid on sugar, starch, and many other organic compounds; also by the action of hypermanganate of potash on sugar, &c.

To prepare it, one part of pure starch is gently heated with 8 parts of nitric acid, Sp. G. 1.20 or 1.25. A very energetic reaction ensues, and much nitrous acid is disengaged; when this slackens, heat is applied, and continued till no more red vapors appear, when the liquid, if sufficiently evaporated, deposits, on cooling, a large quantity of crystals of hydrated oxalic acid. These are dried on a porous tile, to remove the mother liquor which contains much free nitric acid, saccharic acid, and other products. The dried crystals being dissolved in a little hot water, the solution, on cooling, deposits pure oxalic acid in four-sided prisms, which are colorless, very acid, very soluble in hot water, moderately so in cold water. These crystals contain 3 eq. of water of crystallization, $C_2 O_2$, $H O + 3 aq$. When sharply heated, a part sublimes as dry acid, $C_2 O_2$, $H O$. Oxalic acid is destroyed by heat without blackening, which serves to distinguish it from most other organic acids.

It is very poisonous, and is the cause of many fatal accidents from its similarity to Epsom salts, from which, however, it is easily distinguished by its very sour taste. The best antidote is prepared

chalk administered in water, which forms the insoluble and inert oxalate of lime. It is easily detected by forming with lime-water, or a soluble salt of lime, if no free acid be present, the very insoluble oxalate of lime, which when dried and heated to low redness is converted, without blackening, into carbonate of lime.

When oxalic acid, or any of its salts, is heated with oil of vitriol in excess, a brisk effervescence takes place, and the gas given off is a mixture of equal volumes of carbonic acid and carbonic oxide. This character furnishes another good means of recognizing oxalic acid. The reaction is very simple, for $C_2O_3, H_2O + H_2SO_4 = (SO_3 + 2H_2O) + CO + CO_2$. The sulphuric acid seizes the whole of the water, and the anhydrous oxalic acid, C_2O_3 cannot exist in the separate state.

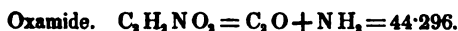
When the oxalates of certain protoxides, as those of cobalt and nickel, are heated in close vessels, the metal is left; carbonic acid being given off: $CoO, C_2O_3 = Co + 2CO_2$. Other oxalates, as that of manganese, give off carbonic acid and carbonic oxide, leaving the protoxide of the metal, $MnO, C_2O_3 = MnO + CO + CO_2$.

Oxalic acid forms salts with bases, many of which are insoluble. The insolubility of the oxalate of lime renders oxalic acid useful as a test for lime, and as a means of separating it, and determining its quantity, in analysis. As a test, it is commonly used in the form of oxalate of ammonia. It can only detect lime in neutral or alkaline fluids, the oxalate of lime being soluble in free acids.

The formation of oxalic acid by the action of oxidizing agents on organic matters, is a partial oxidation of their carbon; when that oxidation is complete, carbonic acid is the result. The action of nitric acid on starch or sugar is complicated, and not so well understood as to admit of being expressed in the form of an equation; but the oxidation of sugar by permanganate of potash is very simple, and is thus represented, $C_{12}H_{10}O_{10} + 6(KO, Mn_2O_7) = 6(KO, C_2O_3) + 10H_2O + 12MnO_2$; that is, 1 eq. of anhydrous sugar, with 6 eq. of the permanganate, produces 6 eq. of oxalate of potash, 10 eq. of water, and 12 eq. of peroxide of manganese.

The most important oxalates are those of potash, lime, and ammonia. There are three oxalates of potash; the neutral oxalate, $KO, C_2O_3 + aq.$; the binoxalate, $KO, C_2O_3 + H_2O, C_2O_3 + 2aq.$; and the quadroxalate, $KO, C_2O_3 + 3(H_2O, C_2O_3 + 4aq.$ The double oxalate of potash and oxide of chromium, described by me some years since, forms crystals which are black by reflected, deep blue by transmitted light. The solution is green and red at the same time by day-light, crimson red by candle-light. Sir D. Brewster has described, in the *Edin. Phil. Trans.*, the very remarkable optical properties of this salt. The oxalate of lime is

$\text{Ca O, C, O}_2 + 2 \text{ aq.}$ The oxalate of silver $\text{Ag O, C}_2 \text{ O}_2$, detonates when heated, yielding, like several other oxalates of the noble metals, carbonic acid, and the metal. The oxalate of ammonia, $\text{N H}_4 \text{ O, C}_2 \text{ O}_2 + \text{aq.}$ is much used as a test. It crystallizes very readily. When heated, it gives rise to a very remarkable compound, namely, *oxamide*, which is the type of a class. We shall here consider it.



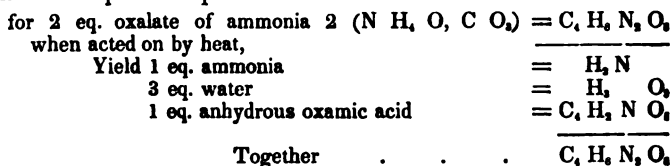
When oxalate of ammonia is heated in a retort, it gives rise to a variety of products, and among these, to a white crystalline powder, insoluble in cold water, which is oxamide. It may be formed far more abundantly by the action of ammonia in solution on oxalate of oxide of ethyle, or oxalic ether. (See oxalate of oxide of ethyle.)

The remarkable character of oxamide is, that while itself neutral, and certainly containing neither oxalic acid nor ammonia, it is easily converted into oxalic acid and ammonia by boiling it either with strong acids or strong alkalies. In this reaction the elements of 1 eq. of water are shared between the constituents of oxamide, that is, between the radical $\text{C}_2 \text{ O}_2$, and the radical amide N H_2 ; for oxamide is nothing more than oxalate of ammonia, $\text{N H}_4 \text{ O, C}_2 \text{ O}_2$, minus 2 eq. of water, or $\text{N H}_2, \text{C}_2 \text{ O}_2$. A very small portion of an acid, for example, is sufficient to produce this effect on a large quantity of oxamide; for if the acid we add be neutralized by the ammonia produced, a corresponding quantity of oxalic acid is set free, and acts as any other acid would do. A minute proportion of an acid, therefore, here, appears to exert its influence on an unlimited portion of oxamide, but this is only in appearance. The fact, however, that the presence of a little oxalic acid enables oxamide to decompose water and to produce ammonia and oxalic acid, is very important, and tends to throw light on many similar changes in the organic kingdom, where the agency is not so apparent.

But oxamide is not the only product of the action of heat on oxalate of ammonia; for, besides carbonic acid, carbonic oxide, hydrocyanic acid, water, ammonia, and oxamide, all of which are or may be formed, there is produced, when the heat is so regulated that a honey-yellow residue remains in the retort, a new acid, called *oxamic acid*, which constitutes that residue. It is mixed with a little oxamide, which is, however, left undissolved by hot water, in which the oxamic acid dissolves.

Oxamic acid forms soluble and crystallizable salts, with lime, baryta, ammonia, and oxide of silver. Acids precipitate it from the saturated solution of its compound with ammonia, as a white sparingly soluble powder, the composition of which is $\text{C, H, N O}_2 + \text{aq.}$ Although an acid, this compound exhibits all the relations

of a compound of amide or amidogen, being converted by the action of alcalies at a high temperature into oxalic acid and ammonia. It differs, however, from oxamide in yielding 2 eq. oxalic acid and 1 eq. ammonia; for 1 eq. of oxamic acid, *plus* 3 eq. of water, contains the elements of binoxalate of ammonia: $C_4 O_8, N H_2 + 3 H_2 O = (H_2 O, C_2 O_3) + (N H_2 O, C_2 O_3)$. This also explains its production:



Oxamic acid is certainly a very remarkable compound, being an acid amidide, or at least admitting of being so regarded, $C_4 O_8, N H_2$. There are a few other examples of acid amidides, and we shall soon come to one, namely, *euchronic acid*, which is highly analogous to oxamic acid; being formed by the action of heat on mellitate of ammonia, along with a neutral amidide, *paramide*, similar to oxamide; and as oxamic acid yields acid oxalate, so euchronic acid yields acid mellitate of ammonia when long boiled with water. Cyanic acid may also be considered as, in some sense, an acid amidide; for $C_2 N O, H_2 O = C_2 O_3, N H$; and $C_2 O_3, N H + 2 H_2 O = N H_2, 2 C_2 O_3$; or, as is well known, cyanic acid, in contact with water, produces bicarbonate of ammonia.

Oxamic acid may further be viewed as a coupled oxalic acid, the adjunct in which is oxamide; for $C_4 O_8, N H_2$ is equal to $C_2 O_3 + C_2 O_3, N H_2$. Berzelius adopts this view, and is, generally speaking, favorable to the idea of coupled acids.

An alcoholic solution of oxalic ether, when ammonia is cautiously added till a precipitate of oxamide just begins to appear, yields a very beautifully crystallizable compound, long known as oxamethan, which is nothing else than oxamate of oxide of ethyle (see salts of oxide of ethyle). Its composition is $C_6 H_7 N O_4 = (C_4 H_5) O + C_2 H_2 N O_3$. A similar compound exists with oxide of methyle, and was formerly called oxamethylan.

2. CARBONIC ACID. $C O_2 = 22$.

This acid has been already described, and it is introduced here merely because it is formed by the complete oxidation of carbonic oxide: $C_2 O_2 + O_2 = 2 C O_2$.

CARBONIC ACID AND CHLORINE.

Chlorocarbonic Acid. $C \begin{Bmatrix} O \\ Cl \end{Bmatrix}$ or $C O + Cl = 49.5$.

SYN. *Phosgene Gas*.—When equal volumes of chlorine and carbonic oxide are mixed and exposed to the sun's rays, they combine to form a colorless gas, of a pungent disagreeable smell, which

acts strongly on the eyes. Sp. G. of the gas 3.399. When dissolved in water, it decomposes it, producing carbonic and hydrochloric acids. With alcohol and pyroxilic spirit it produces very remarkable compound ethers, to be afterward described.

With ammonia, this acid forms sal ammoniac, and a white volatile crystalline substance, which is carbamide, $C O, N H_3$, produced as follows:— $C O, Cl + 2 N H_3 = N H_4, Cl + C O, N H_3$.

Under the influence of the mineral acids, carbamide yields ammonia and carbonic acid, $C O, N H_3 + H O = C O + N H_3$.

The chlorocarbonic acid may be considered as carbonic acid $C + \begin{Bmatrix} O \\ O \end{Bmatrix}$ in which half the oxygen has been replaced by its equivalent of chlorine, $C + \begin{Bmatrix} O \\ Cl \end{Bmatrix}$.

CARBONIC OXIDE WITH POTASSIUM.

Oxycarbide of Potassium: Rhodizonic Acid.

When potassium is heated in carbonic oxide gas, combination takes place, and a dark olive powder is formed, composed of carbonic oxide and potassium, in the proportions of $C, O_7 + K_3$, or $7 C O + 3 K$. This substance is formed in large quantity in the preparation of potassium from carbonate of potash and charcoal, and is the source of great loss as well as inconvenience. No such compound is formed with sodium, for which reason that metal may be more cheaply prepared than potassium.

The oxycarbide of potassium, if heated in the air, takes fire, but if exposed to moist air, or placed in water, it is converted into the potash salt of a new acid, rhodizonic acid, hydrogen being disengaged: $C, O, K_3 + 3 H O = C, O_7, 3 K O + H_3$. As this hydrogen, however, is not pure but contains carbon, the reaction is probably more complicated.

All the salts of rhodizonic acid are deep red, and when in crystals, reflect a green light. The rhodizonate of potash, when heated in solution in water, undergoes a very remarkable change, yielding free potash, oxalate of potash, and croconate of potash, the latter being the salt of another new acid containing the same elements as rhodizonic acid, in different proportions; this salt is $C_4 O_4, K O$ or C, O_3, K . The composition of rhodizonate of potash explains this reaction perfectly, for $C, O_7 + 3 K O = K O + K O, C_2 O_3 + K O, C_2 O_4$.

Croconic Acid. $C_4 O_4, H O ?$ or $C_4 O_4, H$.

This acid is named from the yellow color of its salts. It is obtained from the croconate of potash, prepared as above, by the action of fluosilicic acid, which separates the potash. The acid is yellow, soluble in water and alcohol, and crystallizes easily. All its salts are likewise yellow.

The rhodizonic acid, $C, O_7, 3 H O$, may be viewed as a tribasic hydrogen acid, C, O_7, H_3 ; the croconic acid may also be viewed

both as a hydrated oxygen acid, $C_4O_4H_2O$, and as a hydrogen acid, C_4O_4, H . In this last form it connects itself with carbonic oxide as it may be $5C_4O_4 + H$. The same remark applies to another remarkable acid, containing the same elements, namely the mellitic acid.

Mellitic Acid. C_4O_4, H_2O , or C_4O_4, H .

This acid occurs combined with alumina, in a very rare mineral, probably of organic origin, the mellite or honey-stone. The acid is soluble, very sour, and permanent, not being altered by boiling nitric or sulphuric acids, nor by a heat of nearly 580° . The general formula of its salts when dried at 212° , is MO, C_4O_4, H , or HO, C_4O_4, M . The salt of silver, however, at 212° , loses 1 eq. of water, and is left as C_4O_4, Ag_2O , or, C_4O_4, Ag . According to the latter formula, the radical in this salt, heated to 212° , is a form of carbonic oxide, $C_4O_4 = 4CO$.

The crystallized acid C_4O_4, H_2O , or C_4O_4, H , appears to unite with most bases without the separation of water, generally observed when salts are formed. And although the silver salt would seem to contain a different radical, yet it yields, when decomposed, the original mellitic acid. The mellitate of silver may also be looked on as oxalate of silver Ag_2O, C_2O_4 , plus 2 eq. of carbon in the acid Ag_2O, C_4O_4 .

The mellitate of ammonia, NH_4O, C_4H_4 , when heated in a retort, yields several new and remarkable products. When this salt, $NH_4, HO, C_4O_4 = C_4H_4, N_2O_4$ is heated to 320° , it gives off ammonia and water, and there remains a mixture of two new compounds; a soluble one, which contains *euchronic acid*, in combination with ammonia, and an insoluble one which is called *paramide*.

Paramide is a yellow solid, like clay. Its most remarkable character is, that when long boiled with water, it is converted into bimellitate of ammonia. This is the character of an amide, hence its name. The composition of paramide is $C_4H_4N_2O_4$, which readily explains both its formation, and its conversion into bimellitate of ammonia.

If from bimellitate of ammonia, $NH_4O, C_4O_4 + HO, C_4O_4 = C_4H_4, N_2O_4$, we subtract 4 eq. of water H_2O ,

there will remain Paramide = $C_4H_4NO_4$,

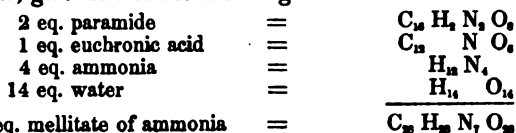
and of course, when reconverted into bimellitate of ammonia by long boiling, it merely takes up again these 4 eq. of water.

The soluble compound *euchronate* of ammonia, when its solution is acted on by hydrochloric acid, deposits a white crystalline powder, which is *euchronic acid*, $C_{12}N_2O_4, 2H_2O$. Its formation is easily explained; for

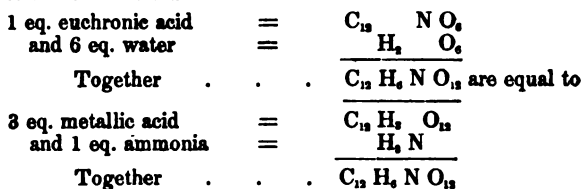
if from 3 eq. mellitate of ammonia, = $3 (C_6 H_4 NO_3) = C_{18} H_{12} N_3 O_9$
 we subtract 6 eq. water and 2 eq. ammonia . . . = $\frac{H_{12} N_3 O_4}{C_{18} H_{12} N_3 O_9}$

There will remain anhydrous euchronic acid . . . = $C_{18} N O_5$

We can now see that the action of heat on 7 eq. of mellitate of ammonia, gives rise to the following substances:



When euchronic acid is boiled with water, it is dissolved and converted into an acid mellitate of ammonia.



Euchronic acid is deoxidized by a plate of zinc, yielding a powder of a fine deep blue color, which dissolves in ammonia, or potash, with a splendid tint of purple. The blue powder is an inferior oxide of the same nitrogenized radical, which, combined with more oxygen, forms euchronic acid. The whole subject of mellitic acid and euchronic acid is most interesting, but mellitic acid is so rare that it is very difficult to find material for the investigation. As mellitic acid, like succinic acid, is of organic origin, and contains only 1 eq. of hydrogen less, and 1 eq. of oxygen more than succinic acid, we may hope to be enabled to obtain it artificially.

III. CYANOGEN. $C_2 N = Cy = 26.23$.

This very important compound has already been mentioned as a compound of carbon and nitrogen; but we have now to consider it in its far more important character of a compound radical. In fact, it was the first compound radical discovered, and the discovery of cyanogen by Gay-Lussac has proved more fertile in results than any other discovery yet made in organic chemistry. As cyanogen acts exactly like an element, we shall represent it by the symbol Cy, rather than by $C_2 N$; using the latter only where the elements of cyanogen, and not itself, enter into changes and reactions.

Cyanogen is formed when animal matter is ignited along with carbonate of potash in close or covered iron vessels. The cyanogen being a gas, and combustible, would be dissipated, and in open vessels burned, were it not that it enters into combination with

potassium derived from the carbonate, forming cyanide of potassium, $K\text{Cy}$, a salt not altered by a red-heat in close vessels. As this salt, however, is decomposed by the action of water, yielding carbonate of potash, and of ammonia, hydrogen being set free, $(K, C, N + 5 H O = K O, C O_2 + N H_3, H O, C O_2 + H)$, it is necessary to convert the cyanide of potassium into a more stable compound.

This is effected by the addition of iron, or of sulphide of iron, the latter of which is formed by the mutual action of the sulphate of potash (always present in potashes), carbon, and the iron of the vessel. The iron, or its sulphide, is readily dissolved by the aqueous solution of cyanide of potassium, yielding cyanide of iron, $Fe\text{Cy}$, and sulphide of potassium $K\text{S}$, for $K\text{Cy} + Fe\text{S} = Fe\text{Cy} + K\text{S}$. The elements of the cyanide of iron then form, with cyanide of potassium, the very permanent double cyanide, well known as prussiate of potash, properly ferrocyanide of potassium, which forms large and pure transparent yellow crystals. From this compound, all the other compounds of cyanogen, and cyanogen itself are prepared. Its empirical formula is $Fe\text{Cy}$, $2 K\text{Cy} + 3 H O$, or $Fe K_2\text{Cy}_2 + 3 H O$. At 212° it loses all the water, and then contains only iron, potassium, and cyanogen, $Fe + K_2 + Cy_2$. It may be conveniently viewed as a compound of cyanide of iron with cyanide of potassium; but we shall see hereafter that its rational formula is probably very different, and that it is a compound of potassium with a new radical, ferrocyanogen.

Cyanogen gas is best prepared by heating dried bicyanide of mercury, when the gas is given off, a part, however, assuming the solid form, and remaining behind as a black matter, paracyanogen, isomeric with cyanogen; or by heating a mixture of 6 parts dried ferrocyanide of potassium, and 9 parts bichloride of mercury, when chloride of potassium is formed by the action of the bichloride on the cyanide of potassium of the ferrocyanide, and the cyanide of mercury, if formed, is at once decomposed by the heat: $Fe\text{Cy}, 2 K\text{Cy} + Hg\text{Cl}_2 = Fe\text{Cy}, 2 K\text{Cl} + Hg + Cy_2$. The cyanide of iron is not altered. The gas may be collected over mercury, but is absorbed by water, with which it produces the various changes which have been minutely explained at pp. 275 and 276. It has a very pungent and peculiar smell, is colorless and transparent; and may be liquefied by a pressure of about 4 atmospheres. It is combustible and burns with a beautiful pink or purplish flame.

Cyanogen forms with hydrogen an acid, the hydrocyanic, $H\text{Cy}$; with oxygen and the elements of water, three acids, $Cy O$, $H O$; $Cy, O_2, 2 H O$; and $Cy, O_2, 3 H O$; of which the first is cyanic, the second fulminic, and the third is cyanuric acid. With chlorine, &c. it combines; with sulphur, it forms a new radical $Cy S_2$.

sulphocyanogen; and with metals, it forms salts, perfectly analogous with chlorides, such as K Cy, Fe Cy, Ag Cy, Hg Cy, &c. In short it plays exactly the part of a simple radical, and were it not easily decomposable, we should at once class it with chlorine as an element.

CYANOGEN AND HYDROGEN.

Hydrocyanic or Prussic Acid. $\text{H Cy} = 27.23$.

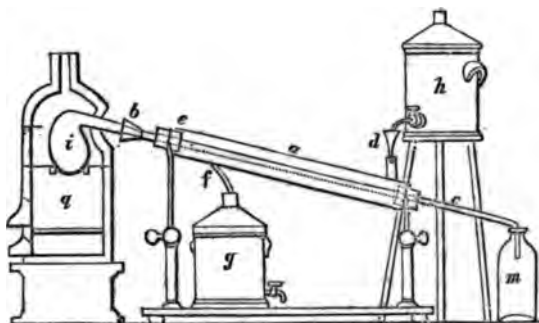
This acid may be obtained by a great variety of processes; but the easiest, most economical, and most certain, is to act on the ferrocyanide of potassium with diluted sulphuric acid. The process requires to be slightly modified, according as our object is to prepare the dry or anhydrous acid, or the diluted aqueous solution of it used in medicine.

1. *Anhydrous Acid*.—To prepare this acid 15 parts of powdered ferrocyanide of potassium are to be distilled at a gentle heat with a mixture of 9 parts oil of vitriol, and 9 of water, and the product is to be received in a convenient receiver placed in a freezing mixture and containing 5 parts of chloride of calcium in small lumps. As soon as liquid enough has distilled to cover the chloride, the distillation is stopped, and the hydrocyanic acid, deprived of water by the chloride of calcium, is to be decanted into a dry and well-stopped bottle. It may also be obtained by distilling, under similar circumstances, cyanide of potassium with dilute sulphuric acid. In both cases, the acid is formed by the reaction of sulphuric acid on cyanide of potassium or its elements: $\text{K Cy} + \text{H, S O}_4 = \text{K, S O}_4 + \text{H Cy}$.

Dry hydrocyanic acid is a limpid and colorless liquid, of Sp. G. 0.6967 at 66° ; at 59° it becomes a fibrous mass, in consequence of the presence of a trace of water; and at 80° it boils; the density of its vapor is 0.9476. It is inflammable, and has a very peculiar and disagreeable smell and taste. It is the most energetic poison known, one drop introduced into the mouth being sufficient to destroy an animal of considerable size. When pure it is soon spontaneously decomposed, depositing a dark brown solid; a trace of sulphuric acid causes it to keep perfectly. When in contact with the strong mineral acids and water, being converted into ammonia and formic acid: $\text{H, C}_2\text{N} + 4 \text{H O} = \text{N H}_3, \text{H O} + \text{C, H O}_2$.

2. *Medicinal or Diluted Hydrocyanic Acid*.—This may be prepared by simply diluting the anhydrous acid with the required proportion of water, adding for example, 97 grains of water to 3 of the acid, to obtain an acid of 3 per cent.; which is about the average strength used in medicine. In round numbers, to one part, by weight, of dry acid, $32\frac{1}{2}$ parts of water by weight are to be added; or, to one volume of the anhydrous acid, $22\frac{1}{2}$ volumes of water. But as it is troublesome to prepare the anhydrous acid,

it is best to distil 2 parts of ferrocyanide, with 1 of sulphuric acid, and 2 of water, to dryness in a chloride of calcium bath, condensing in a Liebig's apparatus, (see wood-cut) in the receiver of which



2 more parts of water are placed. By this means we obtain $4\frac{1}{2}$ parts of an acid not anhydrous, but far too strong for use, containing from 15 to 20 per cent. of dry acid. Its precise strength is ascertained, and it is reduced to the standard strength in the following simple manner:

Any convenient quantity, say 50 or 100 grains, is weighed out, being added to a counterpoised vessel, containing about two drachms of nitrate of silver, dissolved in 2 or 3 ounces of water. Let us suppose that we have dropped into this vessel 70 grains of our acid. This will be entirely converted into cyanide of silver, but we make sure by testing with a drop of nitrate of silver. The precipitate is then collected on a filter, well washed, dried at 212° on a weighed filter, and the increase in weight of the filter gives the weight of the cyanide of silver formed. Now this cyanide is formed as follows: $\text{H Cy} + (\text{Ag O, N O}_3) = \text{Ag Cy} + (\text{H O, N O}_3)$. Therefore 1 eq. of hydrocyanic acid, $\text{H Cy} = 27.23$, produces 1 eq. cyanide of silver, $\text{Ag Cy} = 134.54$; or 1 grain of anhydrous hydrocyanic acid will yield, almost exactly, 5 grains of cyanide of silver; for $27.23 : 134.54 :: 1 : 4.94$. We may, therefore, safely assume that the weight of the cyanide of silver, divided by 5, gives the weight of anhydrous acid present with sufficient accuracy for all practical purposes. Now we have used 70 grains of our dilute acid, the strength of which we wish to know. Let us suppose that our filter weighs when empty 20 grains, and with the cyanide of silver, dried at 212° till it ceases to lose weight, 100 grains. The difference, or 80 grains, is the weight of cyanide of silver obtained from 70 grains of our acid. Dividing this by 5, we have 16 grains as the weight of anhydrous acid contained in the 70 grains, and consequently combined with 54 of water.

Now, if we wish to state the per centage of this acid, we obtain it by the calculation, $70 : 16 :: 100 : x$, and $x = \frac{16 + 100}{70} = 22.85$,

so that our acid contains 22.85 per cent. of anhydrous acid. But if our only object be to reduce the acid to a standard strength, say that of 3 per cent., this last calculation is unnecessary, and we can proceed as follows: acid of 3 per cent. contains 3 grs. of dry acid and 97 of water; therefore, to find how much water is to be added

to 16 grs. of anhydrous acid, $3 : 97 :: 16 : x$, and $x = \frac{97 + 16}{3} =$

517.3 grains of water, which must be added to 16 grs. of anhydrous acid, to bring it to the same strength. But our 70 grains of acid contain already, with the 16 of anhydrous acid, 54 grains of water, consequently we have only to add to these 70 grains $517.3 - 54 = 463.3$ grains of water, and the same quantity of water for every 70 grains of the same acid. Of course, it is easy to calculate the water necessary for 1 or more ounces of the acid, when we have once found it for any given quantity. I have here supposed 70 grains, but with 50 or 100 the calculation is easier, and with a drachm by weight (60 grains), we have simple data for calculating how much water is required for any number of ounces or drachms, troy, of acid.

This beautiful and simple method of preparing the medicinal hydrocyanic acid, and ascertaining its precise strength, has been minutely described, because of its practical importance. It is so simple an operation, that any one may very soon learn to ascertain the strength of hydrocyanic acid, and it is very exact. Besides, no other method of obtaining a medicinal acid of uniform strength ought to be trusted to; and we ought never to attempt to obtain the acid of the standard strength by distillation, although many methods are given for this. I have never seen any one of these yield twice the same result; whereas by the above method we can prepare acid of exactly the same strength any number of times, and the acid prepared from the ferrocyanide, by sulphuric acid, keeps perfectly well. Of course, when we have added the calculated quantity of water to reduce the acid, it is proper to ascertain its strength once more, to make sure that we have made no error in our calculation. If it be acid of 3 per cent., it will yield 15 grains of cyanide of silver from 100 of acid.

There are two other methods which deserve to be mentioned, as, with pure materials and careful manipulation, they yield, in a few minutes, a standard acid. The first is that of Dr. Clarke, who adds to 1 eq. cyanide of potassium dissolved in water, 2 eq. tartaric acid, which separates the potassium as cream of tartar, while diluted hydrocyanic acid remains dissolved. For every 100 grs. of water, $7\frac{1}{2}$ grs. of cyanide of potassium and $16\frac{1}{2}$ of crystallized

tartaric acid, are required. This is an excellent extemporaneous process, if we have pure cyanide of potassium; but that salt does not keep well, and even in its preparation it is apt to be decomposed, at least partially. It is, besides, an expensive salt. The other is the process of Everett, who suspends cyanide of silver in water, and adds an equivalent of hydrochloric acid: $\text{Ag Cy} + \text{H Cl} = \text{Ag Cl} + \text{H Cy}$. This is also a good extemporaneous process, 15 grs. of Ag Cy being used for every 100 of water, and 4 grs. of dry H Cl, that is, about 12 grs. of acid Sp. G. 1.21, being added. This process is also expensive, although the silver is not lost; but the chief objection is, that it is difficult to add the precise amount of hydrochloric acid which is necessary, and that an excess causes, *pro tanto*, a conversion of the hydrocyanic acid into formic acid and ammonia.

The medicinal acid has the smell and taste of the anhydrous, and is very poisonous, the average dose safe for an adult being 1 to 2 drops in a glass of water. It is much used as a sedative and anodyne, but, unless its strength and dose be perfectly known, it is a dangerous remedy. Fatal accidents have occurred from prescriptions, found, after experience, to act favorably, being made up in another place, or by the same druggist with a fresh stock; this fresh stock being exactly of the standard strength, while the previous acid had lost so much by keeping that the dose had been of necessity increased. There, danger actually arose from a too weak acid being used. Hence the necessity for the great exactness, for which rules are given above. In cases of poisoning by this acid, now unfortunately of very frequent occurrence, there is seldom time to administer an antidote; but when life is not extinct, we may confidently rely on the antidotes we possess. The best is the administration of two solutions, one of mixed sulphate of protoxide and peroxide of iron, and the other of carbonate of potash, as recommended by Messrs. Smith, Edinburgh,* by which the acid still in the stomach is rendered insoluble, being converted into Prussian blue. The symptoms already produced are best combated by ammonia inspired from a sponge, or taken, diluted, internally, and by other diffusible stimulants; also by the cold affusion.

Hydrocyanic acid is very easily recognized by its smell, and by its forming Prussian blue if acted on, in solution, successively, by proto-persulphate of iron, by potash, and by an excess of hydrochloric acid. The first two tests form the Prussian blue; the last, dissolving the excess of oxide of iron, brings the blue into view. Any liquid, suspected to contain hydrocyanic acid, ought first to be distilled with the addition of a little dilute sulphuric acid, and the tests applied to the first ounce that comes over. Nitrate of

* See "Lancet," for 1844, vol. ii. p. 41.

silver produces a white cloud of cyanide of silver, exactly like the chloride in appearance.

Hydrocyanic acid, with metallic oxides, gives rise to water and metallic cyanides: $\text{H Cy} + \text{M O} = \text{H O} + \text{M Cy}$: or $2 \text{H Cy} + \text{M O}_2 = 2 \text{H O} + \text{M Cy}_2$.

CYANOGEN AND OXYGEN.

1. CYANIC ACID. $\text{Cy O}, \text{H O} = \text{Cy O}, \text{H} = 43.25$.

A monobasic acid; is formed when dry cyanide of potassium is heated in the air, when oxygen is absorbed, and cyanate of potash is produced: $\text{K Cy} + \text{O}_2 + \text{K O}, \text{Cy O}, \text{or K}, \text{Cy O}_2$.

When a stronger acid is added to this salt, the cyanic acid is set free, but immediately decomposes with water, producing ammonia which unites with the strong acid used, and carbonic acid which escapes as gas: $\text{C}_2 \text{N O}, \text{H O} + 2 \text{H O} = \text{N H}_3 + 2 \text{C O}_2$. The carbonic acid carries with it a little cyanic acid, which forms dense white vapors, and has a pungent acid smell like that of strong acetic acid. Under all circumstances, free cyanic acid, in contact with water, is instantly destroyed.

It may, however, be obtained in the anhydrous state, according to the formula $\text{Cy O}_2 + \text{H}$, or as monohydrated acid, if viewed as $\text{Cy O}, \text{H O}$, by distilling cyanuric acid, $\text{C}_3 \text{O}_6 + \text{H}_2$, or $\text{Cy}_2 \text{O}_3 + 3 \text{H O}$. This acid is isomeric with cyanic acid, and when heated, 1 eq. cyanuric acid splits up into 3 eq. cyanic acid, which appears in the receiver as a volatile, pungent, very corrosive acid liquid. This acid only keeps for a very short time, even in the freezing mixture in which it is condensed. If removed from the cold, it soon becomes turbid, then hot, boils violently, and with violent shocks, and is converted into a solid dense white body, like porcelain, quite insoluble and indifferent.

This is *Cyamelide*, another isomeric compound, containing the same elements in the same proportions, but differently arranged, possibly $\text{C}_2 \text{O}_3 + \text{N H}$; for it yields, under the influence of water and strong acids, carbonic acid and ammonia, $(\text{C}_2 \text{O}_3, \text{N H} + 2 \text{H O} = 2 \text{C O}_2 + \text{N H}_3)$, just as cyanic acid does. When distilled, it is reconverted into cyanic acid, another proof that it is isomeric with that acid.

CYANATES.

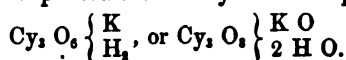
The salts of cyanic acid are all distinguished by the action on them of strong acids, which cause disengagement of carbonic acid, while ammonia may now be detected in the liquid. The cyanates of potash, ammonia, &c., are soluble, those of lead, silver, &c., insoluble.

Cyanate of Potash—Is best formed by the oxidation of Liebig's cyanide of potassium,* which may easily be effected by adding

* The formation of this salt will be described below

litharge in proper quantity to the melted salt, $K\ Cy + 2\ Pb\ O = K, Cy\ O_2 + Pb_2$. The cooled mass is powdered and boiled with alcohol of 80 per cent., which on cooling deposits pure crystals of cyanate of potash, very similar to chlorate of potash. Or dried ferrocyanide of potassium, mixed with half its weight of peroxide of manganese, may be gently heated, spread out on an iron plate, when it burns like tinder, partly at the expense of the oxide of manganese, partly in the oxygen of the air. It is well stirred till every part has glowed, and the cold mass is treated with alcohol as above.

Cyanate of potash must be kept in sealed tubes, for in phials occasionally opened it is soon changed into bicarbonate of potash, ammonia being given off: $K, C_2\ N\ O_2 + 3\ H\ O = (K\ O_2, 2\ C\ O_2) + N\ H_3$. Triturated with dried oxalic acid, this salt yields oxalate of potash and cyamelide. When acetic acid is added to a concentrated freshly made solution of cyanate of potash, the latter being in excess, there is deposited the acid cyanurate of potash.



CYANATE OF AMMONIA.

a. *Basic*.—When dry ammonia and the vapor of cyanic acid are mixed, they form a light white solid, which is a cyanate of ammonia, containing more ammonia than is required for a neutral salt. This salt gives off ammonia when treated with alcalies, and cyanic acid when treated with sulphuric acid. But if dissolved in water, and the solution digested and evaporated, it yields crystals, which, although containing the elements of cyanic acid, ammonia, and water, exhibit neither of these characters of a cyanate, but are found to possess all the properties of *urea*, a product of the animal system.

b. *Anomalous Cyanate of Ammonia*, or *urea*, $C_2\ N_2\ H_4\ O_2 = (C_2\ N\ O, H\ O, N\ H_3)$.—This remarkable compound exists in large proportions in healthy urine, and is extracted from it by evaporating it about 200° to a thin syrup and adding about an equal volume of colorless nitric acid, Sp. G. 1.35, quite free from nitrous acid, which forms a very copious crystallization of nitrate of urea, while the coloring matter is destroyed with brisk effervescence. If cold be applied, the coloring matter resists, and the nitrate is then very dark and very difficult to purify; cold ought therefore not to be used, and the nitrate of urea is deposited nearly white, having only a clear yellow tint. It is dissolved in water, after being recrystallized and neutralized by potash or baryta. The whole is then gently evaporated to dryness, after separating as much nitrate of potash or of baryta as possible, and the dry mass digested in alcohol, which dissolves only the urea, and by spontaneous evaporation, yields it in large transparent prismatic crystals. Should

these not be colorless, the digestion of their aqueous solution with a little permanganate of potash, which has no action on urea, destroys the coloring matter entirely. Should an excess of that salt be added, a few drops of alcohol will instantly destroy it, and the filtered liquor will yield snow-white crystals of urea.

But although urea may thus be obtained (or by the action of oxalic acid on the urine, which forms a sparingly soluble oxalate of urea) in an any quantity from urine, it is found much easier to prepare it artificially from cyanate of ammonia. Liebig recommends the following process, which I have found to succeed perfectly: 28 parts of dried ferrocyanide of potassium, and 14 of peroxide of manganese are mixed in powder and calcined, as above described, on a flat iron plate, at a very low red-heat, sufficient to keep up the glow which takes place. When this is over, the cold mass, powdered, is acted on by a moderate quantity of cold water, which dissolves the cyanate of potash. This is filtered off and set aside. A fresh portion of cold water being added to the powder to wash it, is also filtered, and in this liquid are now dissolved 20½ parts of sulphate of ammonia, and the solution is added to the first filtered solution of cyanate. A large quantity of sulphate of potash is deposited, which is strained off, and the filtered liquid now containing, with some sulphate of potash, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia is transformed into urea. The dry mass is digested in alcohol, which dissolves only the urea, and yields it from the first chemically pure and in any quantity, if the operation be carefully performed. Urea thus obtained is far cheaper than that extracted from the urine.

The artificial production of urea from cyanate of ammonia was discovered by Wöhler. It was, with the exception of oxalic acid, and of hydrocyanic acid, the first example of an organic product artificially formed, although many other cases are now known.

Urea forms four sided prisms, resembling nitre in appearance, and also in their taste, which is saline and cooling exactly like that of nitre. It is soluble both in water and alcohol. When heated, it melts, gives off much ammonia, and finally solidifies, being in a great measure converted into ammonia and cyanuric acid.

Urea belongs to the class of organic bases, for it forms crystallizable compounds with several acids, such as nitric, oxalic, and acetic acids.

The nitrate, when impure, crystallizes in scales of a high lustre; when pure, it forms opaque prisms, or a crystalline powder. It is sparingly soluble in cold water, but very soluble in hot water. Formula, $(C, N, H, O, H O, N O_2)$.

The oxalate forms long transparent prisms, very sparingly soluble. Formula, $(C, N, H, O_2, H O, C, O_2) = C, N, H, O_2$.

The acetate I have obtained, as a mass of prismatic crystals, exceedingly soluble in water. Formula, probably, $(C_2 N_2 H_4 O_8, H_2 O, C_2 H_3 O_2) = C_2 N_2 H_3 O_4$.

Although urea combines with pure nitric acid, it is instantaneously decomposed by hyponitrous acid, yielding ammonia, water, and equal volumes of carbonic acid and nitrogen gases: $C_2 N_2 H_4 O_2 + N O = N H_3 + H_2 O + 2 C O_2 + N_2$. When acted on by strong acids or alkalies, with the aid of heat, urea takes up the elements of water and forms carbonate of ammonia: $C_2 N_2 H_4 O_2 + 2 H_2 O = 2 (N H_3, C O_2)$. When urine is left in contact with the mucus usually suspended in it, the mucus entering into decomposition excites in the urea such a reaction with the elements of water, as very soon to convert the whole urea into carbonate of ammonia. Hence the reason why urine soon becomes alkaline, even if acid when voided. But if filtered from the mucus as soon as passed, it keeps unchanged, in clean vessels, for a long period.

2. FULMINIC ACID. $Cy_2 O_2, 2 H_2 O = Cy_2 O_4, H_2 = 86.5$.

A bibasic acid, unknown in the separate form. It is obtained in combination with oxide of mercury, or oxide of silver, by treating alcohol with the nitrates of these metals, and free nitric acid. A violent effervescence takes place, dense white vapors are disengaged, and a crystalline powder is deposited, which is fulminate of mercury or of silver. Both detonate powerfully by heat, friction, or percussion.

In the above reaction there are first formed, on the one hand, hyponitrous acid; on the other, aldehyde, and formic and oxalic acids. The fulminic acid is the result of a reaction between oxide of ethyle (ether) and hyponitrous acid, in presence of oxide of mercury or oxide of silver: $2 N O_2 + (C_2 H_5) O = C_2 N_2 O_2 + 5 H_2 O = Cy_2 O_2, 2 H_2 O + 3 H_2 O$.

This acid cannot be isolated, being instantly decomposed when deprived of a fixed base. It forms two series of salts; neutral, with 2 eq. of fixed base, $Cy_2 O_2, 2 M O$; and acid with 1 eq. of fixed base and 1 of water $Cy_2 O_2, \begin{Bmatrix} H O \\ M O \end{Bmatrix}$. It also forms salts with 1 eq. of two different bases, of which one is always easily reducible, as oxide of silver, mercury, and copper, while the other may be difficult to reduce, such as baryta, potash, &c.

The fulminates of silver and mercury, $Cy_2 O_2, 2 Ag O$, and $Cy_2 O_2, 2 Hg O$, are examples of the first class. The acid fulminate of zinc, $Cy_2 O_2, \begin{Bmatrix} H O \\ Zn O \end{Bmatrix}$, formerly supposed to be fulminic acid, is an example of the second; and the double fulminates of copper and silver, and of potash and silver, $Cy_2 O_2, \begin{Bmatrix} Cu O \\ Ag O \end{Bmatrix}$, and $Cy_2 O_2$

$\left\{ \begin{array}{l} \text{K O} \\ \text{Ag O} \end{array} \right.$ are examples of the third. No neutral fulminates exist with 2 eq. of a difficultly reducible oxide, such as potash, soda, baryta, &c.: nor do any acid fulminates occur with such bases. These very remarkable facts evidently point to some relation, not yet understood, between the oxygen of the base in a salt and the acid of that salt. Of course all the above formulæ may be written according to the theory of compound radicals and hydrogen acids.

To prepare the fulminate of mercury, which is much used for percussion caps, 1 part of mercury is dissolved in 12 parts of nitric acid, Sp. G. 1.36; 11 parts of alcohol at 80 per cent. are added, and the whole is warmed. A brisk reaction soon ensues, very thick white vapors are given off, and the salt is deposited in crystalline grains, mixed with a little metallic mercury. This salt explodes by friction, by percussion, or by heat, and it is a dangerous product, exploding occasionally without apparent cause. An explosion of this nature, not long since, destroyed the distinguished chemist, Mr. Hennell, who was preparing a large quantity in the open air. The fulminate of silver is prepared in the same way, only with 10 parts of nitric acid and 20 of alcohol. Caustic alkalies precipitate from its solution half the silver, forming double fulminates; and chlorides also only precipitate half the silver. Nitric acid, added to the solution, causes a deposit of acid fulminate of silver, $\text{Cy}_2 \text{O}_3 \left\{ \begin{array}{l} \text{H O} \\ \text{Ag O} \end{array} \right.$, or $\text{Cy}_2 \text{O}_4 \left\{ \begin{array}{l} \text{H} \\ \text{Ag} \end{array} \right.$.

Hydrochloric acid added to fulminate of silver, gives rise to water, chloride of silver, hydrocyanic acid, and a new acid, chlorohydrocyanic acid, $\text{C}_2 \text{N Cl}_2, \text{H}_2$. Thus, $\text{C}_2 \text{N}_2 \text{O}_3, 2 \text{Ag O} + 7 \text{H Cl} = 4 \text{H O} + 2 \text{Ag Cl} + \text{C}_2 \text{N H} + \text{C}_2 \text{N Cl}_2, \text{H}_2$.

3. CYANURIC ACID. $\text{Cy}_2 \text{O}_3, 3 \text{H O} = \text{Cy}_2 \text{O}_4, \text{H}_2 = 126.75$.

A tribasic acid discovered among the products of the distillation of uric acid. It is formed when solid chloride of cyanogen, $\text{Cy}_2 \text{Cl}_2$, acts on water: $\text{Cy}_2 \text{Cl}_2 + 6 \text{H O} = 3 \text{H Cl} + \text{Cy}_2 \text{O}_3, \text{H}_2$. It is also formed when urea is heated so as to expel its ammonia. According to what has been stated of the composition of urea, it ought to yield cyanic acid when deprived of its ammonia; but at that temperature 3 eq. of cyanic acid, $3 \text{Cy O}, \text{H O}$, coalesce to form 1 eq. of cyanuric acid, $\text{Cy}_2 \text{O}_3, 3 \text{H O}$. When, again, ascetic acid is added to cyanate of potash, in quantity insufficient to decompose the whole, there is deposited a salt which is an acid cyanurate of potash, $\text{Cy}_2 \text{O}_3 \left\{ \begin{array}{l} \text{K O} \\ 2 \text{H O} \end{array} \right.$.

Finally, cyanuric acid is obtained by dissolving melame, ammeline, ammelide and melamine (see those substances) in sulphuric acid, and diluting and heating the solution, until it yields no precipitate with ammonia. On evaporation and cooling, the acid

forms prismatic crystals, which are $Cy, O_3, 3 H O + 4 aq.$ When dissolved in hot nitric or hydrochloric acid, it is deposited, on cooling, in anhydrous octahedrons. When it has been prepared by heating urea, it is purified by dissolving it in oil of vitriol, and adding nitric acid, drop by drop, till the color is entirely destroyed. An equal bulk of water is then added, and on cooling, pure cyanuric acid is obtained in crystals.

Cyanuric acid has a weak acid taste, and is sparingly soluble in cold water, more soluble in hot water. Unlike cyanic and fulminic acids, it is very permanent in the uncombined state. When heated in close vessels, it is entirely volatilized in the form of cyanic acid, of which 3 eq. are exactly equal to 1 eq. of cyanuric acid.

As cyanuric acid is formed when urea (cyanate of ammonia) is decomposed by heat, and when cyanate of potass is acted on by acetic acid, and as cyanuric acid, when heated, is resolved into cyanic acid, we have every reason to think that in the former cases 3 eq. of cyanic coalesce to form one of cyanuric acid; and that, in the latter case, 1 eq. of cyanuric acid is broken up into 3 eq. of cyanic acid: $3 (Cy O, H O) = Cy, O_3, 3 H O.$

Like other tribasic acids, cyanuric acid forms three series of salts, according to the formulæ:

Hydrated Acid.	Salt with 1 eq. of fixed base.	Salt with 2 eq. of fixed base.	Salt with 3 eq. of fixed base.
$Cy, O_3, 3 H O.$	$Cy, O_3, \left\{ \begin{array}{l} M O \\ 2 H O. \end{array} \right.$	$Cy, O_3, \left\{ \begin{array}{l} 2 M O \\ H O. \end{array} \right.$	$Cy, O_3, 3 M O.$

The salts with 1 and 2 eq. of fixed base are acid; that with 3 eq. is neutral. With potash and other similar oxides, only the two acid salts are known: with oxide of silver, the salts with 2 and 3 eq. of oxide.

The three following salts, namely,

Cyanate of Silver.
 $Cy O, Ag O;$

Fulminate of Silver.
 $Cy, O_3, 2 Ag O;$

Cyanurate of Silver.
 $Cy, O_3, 3 Ag O,$

have exactly the same composition in 100 parts; and yet they are in properties entirely dissimilar; this can only be accounted for by some such difference in their formulæ as is exhibited above. The acids of these salts are all mutually convertible; for when fulminate of silver is decomposed by a salt of ammonia, the fulminate of ammonia is transformed, like the cyanate, into urea; urea, when heated, yields cyanuric acid; and cyanuric acid, when distilled, is transformed into cyanic acid. All these circumstances favor the belief that all three are compounds of cyanogen, and that they differ in the absolute number of equivalents of their elements.

Cyamelide. $C_3 O_3 + N H ?$

But this is not the end of these transformations, for when cyanic acid is left to itself it becomes turbid and hot, and is soon converted with great heat, into an opaque white solid body, cyamelide,

which has no acid properties; and which is also obtained as a white insoluble powder, when fused cyanate of potash is triturated with dried oxalic acid, in which case oxalate of potash is formed, and the cyanic acid, at the moment of being set free, is transformed into cyamelide. Cyamelide is neutral and insoluble in water and acids. It dissolves in aqua potassæ, ammonia being evolved, and the solution yields cyanurate of potash. Heated by itself it yields cyanic acid, which again passes into cyamelide; and when heated with strong sulphuric acid, it forms sulphate of ammonia, while carbonic acid escapes: this action is identical with that which occurs when cyanic acid is acted on by water and by acids. All these observations prove that cyamelide is another isomeric modification of cyanic, fulminic, or cyanuric acid. Its probable formula is $C_2 O_2 + N H$, and this, with 2 eq. $H O$, yields bicarbonate of ammonia, just as cyanic acid, the formula of which is the same, does. The action of potash is probably this: $4 (C_2 O_2 N H) + 3 H O + 4 K O = C_2 N_2 O_6, \begin{cases} 2 K O \\ H O \end{cases} + 2 K O, C O_2 + N H_3$; that is, 4 eq. cyamelide, 3 eq. water, and 4 eq. potash, yield 1 eq. cyanurate of potash, 2 eq. carbonate of potash, and 1 eq. ammonia.

The three oxygen acids of cyanogen may be fitly compared with the three phosphoric acids; and as we have hitherto made use of the older view of these acids, that which makes them hydrated oxygen acid, we shall in this comparison, adopt the other theory, and speak of them as hydrogen acids.

	Monobasic.	Bibasic.	Tribasic.
Acids of cyanogen,	$Cy O_2 + H$	$Cy_2 O_3 + H_2$	$Cy_3 O_4 + H_3$
Acids of phosphorus,	$P_2 O_3 + H$	$P_2 O_5 + H_2$	$P_2 O_5 + H_2$

In the cyanic acids, both the radical and the replaceable hydrogen being doubled and trebled, the capacity of saturation increases in the same ratio. In the phosphoric acids, the capacity of saturation also increases with the replaceable hydrogen, but a great addition to the radical has no corresponding effect in increasing either the replaceable hydrogen or the neutralizing power. Thus, if to tribasic phosphoric acid $P_2 O_5 + H_2$, we add 2 eq. of $P_2 O_3 = P_2 O_5$, we obtain $P_2 O_5 + H_2 = 3 (P_2 O_3 + H)$; that is, the acid becomes monobasic, but the quantity of base neutralized is the same after that addition as before. Notwithstanding this difference, however, the analogy between the monobasic, bibasic and tribasic acids of cyanogen and phosphorus, as well as that between their salts, is most interesting and worthy of attention. As we believe that the phosphoric acids contain three different radicals, $P_2 O_3$, $P_2 O_4$, and $P_2 O_5$, so we may admit that the three cyanic acids have each a distinct radical; only in this case the three radicals are alike in composition, and differ in their relative weight: the first being $C_2 N = Cy$; the second $C_2 N_2 = Cy_2$; and the third $C_2 N_3$.

= Cy_3 ; or, in other words, these radicals are cyanogens, differing in molecular constitution, or three different allotropic forms of cyanogen. The relations of chlorine to cyanogen, and the existence of paracyanogen, countenance this idea.

CYANOGEN AND NITROGEN.

Mellone = $Cy, N = C, N_4 = Me = 93$.

Cyanogen, when it combines with nitrogen in the proportion of 3 eq. Cy to 1 eq. $N = C, N_4$, produces a very remarkable compound, discovered by Liebig, and called mellone, which being itself a well-marked compound radical, will be described as such, and not as a compound of cyanogen and nitrogen.

CYANOGEN AND CHLORINE.

Cyanogen forms two chlorides: one gaseous, but compressible, obtained by the action of chlorine gas on dry hydrocyanic acid; the other solid, formed by a spontaneous transformation of the former when kept in the liquid form in sealed tubes. Both are volatile and both contain cyanogen and chlorine, equivalent for equivalent. But the vapor of the solid chloride is three times denser than that of the other; and, moreover, the solid chloride, in contact with water, produces hydrochloric and cyanuric acids; while the gaseous chloride, under the same circumstances, gives rise to hydrochloric acid, and cyanic acid, the latter with water, at once passing into bicarbonate of ammonia, so that the final result is sal ammoniac and carbonic acid.

These considerations prove that the two chlorides are isomeric; that the first or gaseous chloride is $Cy Cl$; and that the solid chloride is Cy, Cl_3 , and is formed by the junction into one group of 3 eq. of the other; and we are consequently justified in extending this view to cyanic and cyanuric acids, and in supposing the vapor of the latter to be three times more condensed than the vapor of cyanic acid; and the cyanogen of cyanuric acid to be the cyanogen of the solid chloride, and three times denser than ordinary cyanogen.

CYANOGEN WITH BROMINE AND IODINE.

With these elements cyanogen readily combines when cyanide of mercury is distilled with bromine or iodine. The bromide and iodide are both volatile, and crystallizable, pungent and poisonous.

To judge by the density of their vapors, these compounds are $Cy Br$ and $Cy I$, corresponding to the liquid chloride, which is also very pungent and irritating to the eyes.

CYANOGEN AND SULPHUR.

Bisulphide of Cyanogen. $Cy S_2 = 58.5$

When sulphocyanide of potassium, (see that salt), is acted on by chlorine or by dilute nitric acid, there is obtained an orange-yellow

powder, which contains sulphur and cyanogen, and which is supposed by some to be bisulphide of cyanogen, by others to contain hydrogen. This question will be considered hereafter, for whether this be so or not, there is a compound, possibly that compound, of sulphur and cyanogen, which acts as a radical, and is hence called sulphocyanogen. It will be described separately, since it is far more important as a radical than as a compound of cyanogen.

CYANOGEN AND METALS.

With metals, cyanogen forms compounds which in many cases are analogous to the chlorides of the same metal. When the metal is easily reducible, such as silver, mercury, or palladium, the cyanide is formed by the action of hydrocyanic acid on the oxide, or its salts: $M O + H Cy = H O + M Cy$. In the case of difficultly reducible metals, such as potassium, hydrocyanic acid seems to combine with the oxide, not being able to reduce it, until another cyanide is added, which tends to form a double cyanide.

Cyanide of Potassium = $K Cy$ —Is best formed by heating to whiteness in close vessels the ferrocyanide of potassium, a salt which may be viewed as containing cyanide of iron and cyanide of potassium. The former is converted into insoluble carbide of iron; the latter remains unchanged, and may be mechanically picked out, or dissolved by hot alcohol of 60 per cent., which deposits it on cooling. Or, an alcoholic solution of pure and dry hydrocyanic acid is added to an alcoholic solution of potash; or, lastly, the vapors of hydrocyanic acid, formed on the process given at p. 296, are conducted into an alcoholic solution of potash, kept cool, when the salt is deposited.

It is white, and crystallizable in tubes. It has no smell when pure, but when exposed to moist air, smells of hydrocyanic acid. It is very poisonous. When heated it fuses easily, and is not altered by heat in close vessels. Heated in the air it absorbs oxygen, and is converted into cyanate of potash, $K Cy + O_2 = K O, Cy O$. It is very soluble and deliquescent, and its solution, attracting carbonic acid from the air, gives off hydrocyanic acid: hence its smell.

Cyanide of Sodium—Is analogous to the preceding salt.

Cyanide of Zinc, $Zn Cy$ —Is obtained by adding hydrocyanic acid to acetate of zinc. It is a snow-white insoluble powder, which is used in medicine.

Cyanide of Iron.—Protocyanide of iron, $Fe Cy$, has not been isolated. There appears to exist a percyanide, also not yet isolated, Fe, Cy_3 ; and, according to Pelouze, there may be obtained an intermediate cyanide, Fe, Cy_4 , analogous to the magnetic oxide of iron, as a green powder.

But although the cyanides of iron are little known, there are some very important compounds, especially those of two radicals,

which contain those elements, namely, cyanogen and iron, along with hydrogen, and with metals. These will be described after we have gone over the simple cyanides of the metals.

Cyanide of Cobalt, Co Cy.—Is obtained as a brownish white precipitate, by adding hydrocyanic acid to the acetate of cobalt. Cobalt also forms compounds analogous to those of iron above alluded to, with cyanogen, &c.

Bicyanide of Mercury, Hg Cy.—Is easily obtained by dissolving red oxide of mercury in very dilute hydrocyanic acid, till the smell of the acid is destroyed. The liquid, rendered neutral, if necessary, by a few drops of hydrocyanic acid, yields fine crystals, on evaporation and cooling. Or it may be made by the action of three parts of persulphate of mercury on two of ferrocyanide of potassium dissolved in fifteen of hot water, which is boiled and filtered, and the filtered liquid on cooling deposits the bicyanide.

It forms regular prismatic crystals, permanent in the air, of a horrible metallic taste, soluble in water and alcohol. It is used for making cyanogen, also to prepare hydrocyanic acid by one process, and to yield the bromide and iodide of cyanogen.

Cyanide of Silver, Ag Cy.—Formed by the action of hydrocyanic acid or cyanide of potassium on nitrate of silver. It is exactly similar to the chloride, white, curdy, insoluble in water or acids, soluble in ammonia. It is decomposed by hydrochloric acid, yielding hydrocyanic acid.

Cyanide of Palladium, Pd Cy.—The affinity of cyanogen for palladium is most powerful, and hydrocyanic acid, or a soluble cyanide, when added to a salt of oxide of palladium, precipitates the cyanide as a gray powder. This property serves for separating palladium from other metals.

Cyanides of Gold.—The protocyanide, Au Cy, is formed by adding cyanide of potassium in excess to protochloride of gold, till a clear solution is formed, and then adding hydrochloric acid, which precipitates the protocyanide as a bright yellow powder, very permanent, and soluble in cyanide of potassium.

The tercyanide, An Cy,, is formed by the action of cyanide of potassium on terchloride of gold, and appears as whitish-yellow precipitate, soluble in cyanide of potassium, insoluble in acids.

DOUBLE CYANIDES OF THE METALS.

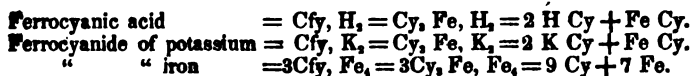
The insoluble metallic cyanides, such as those of iron, cobalt, copper, silver, gold, platinum, and others, dissolve readily in cyanide of potassium, or sodium, forming crystallizable double cyanides, which are not affected by soluble carbonates nor by chlorides, but are generally decomposed by acids, which precipitate the insoluble cyanide. If these double cyanides, which may be $2\text{ K Cy} + \text{m Cy}$ (m Cy, being an insoluble metallic cyanide), are added to the solution of the oxide of another metal forming also

an insoluble cyanide, this latter metal takes the place of the potassium, and a new double insoluble cyanide is the result. Thus, $(2 K Cy + m Cy) + 2 M O = 2 K O + (2 M Cy + m Cy)$. (Here m may be iron and M copper or lead). Now, as these double cyanides, thus precipitated, are of various and often characteristic colors, the ferrocyanide of potassium, $2 K Cy + Fe Cy$, is extensively used as a test for metals.

The protocyanide of iron, the percyanide of iron, the percyanide of cobalt, and perhaps some others, not only form double salts with the elements of cyanide of potassium, but also produce very remarkable acids, by combining with the elements of hydrocyanic acid, that is, with hydrogen replacing the potassium of the double salt. Thus ferrocyanic acid is $2 H Cy + Fe Cy$, and so on. In these compounds the hydrocyanic acid is no longer poisonous, and it is therefore highly probable that these acids, and their corresponding salts, really contain new and very peculiar radicals. The assumption of these radicals will alone enable us to classify or remember these compounds.

IV. FERROCYANOGEN. $Cy, Fe = Cfy = 105.87$.

We assume, then, the existence of this radical as the basis of ferrocyanide of potassium, or prussiate of potash. It is bibasic, combining with 2 eq. of hydrogen or of metals. The following formulæ expresses the composition of ferrocyanic acid, and of ferrocyanide of potassium, &c.



It will be seen, by the two first compounds, that we may consider them either as compounds of the radical Cfy with hydrogen or metals, or as double cyanides. In the third, which is the formulæ of Prussian blue, we see that the iron exists in two different states, in one of which it cannot be detected by the usual tests. That form is the radical Cfy , which exists also in the two preceding compounds.

Ferrocyanic Acid. $Cfy, H_2 = 107.87$.

This very interesting compound is obtained by mixing a cold saturated solution of ferrocyanide of potassium with one-quarter its volume of strong hydrochloric acid, and, agitating the mixture with half its bulk of pure ether: the ether rises to the surface, carrying with it, suspended, a white crystalline substance, which when washed with ether and dried, is ferrocyanic acid. It is soluble in water and alcohol, has a decidedly acid taste and reaction, and decomposes the alkaline carbonates, forming with carbonate of potash the ferrocyanide of potassium. The production of this compound by the action of hydrochloric acid on ferrocyanide of

potassium is very easily explained: $\text{Cfy, K}_2 + 2 \text{ H Cl} = \text{Cfy, H}_2 + 2 \text{ K Cl}$.

Although this compound may be represented as a combination of cyanide of iron with hydrocyanic acid, $\text{Fe Cy} + 2 \text{ H Cy}$, there is every reason to believe that it contains no hydrocyanic acid, as such. For not only is it far more strongly acid, (and protocyanide of iron cannot be supposed to give acid properties to hydrocyanic acid,) but it is totally destitute of all poisonous properties, for both it and its salts may be taken internally without farther effect than the laxative action common to most neutral salts.

Ferrocyanic acid, being bibasic, forms two kinds of salts: in the first the 2 eq. hydrogen are replaced by 2 eq. of potassium, sodium, &c.; in the second they are replaced by equivalents of two different metals, such as potassium and barium. An example of the first class is, $\text{Cfy} + \text{K}_2$; of the second $\text{Cfy} \begin{cases} \text{K.} \\ \text{Ba.} \end{cases}$. Of all these compounds, by far the most important is the ferrocyanide of potassium, or prussiate of potash, from which all the compounds of cyanogen may be prepared, and which is manufactured on the large scale, being also used in the arts.

Ferrocyanide of Potassium. *Syn. Prussiate of Potash.*—Anhydrous, Cfy K_2 , 184.17. Crystallized, it is $\text{Cfy, K}_2 + 3 \text{ H O} = 211.2$. This valuable salt is prepared by infusing animal matter, such as dried blood, hoofs, hair, horns, &c., or the animal charcoal remaining after such matters have been distilled, to obtain carbonate of ammonia, with potashes or pearlash in iron vessels, as long as gas is disengaged. The melted mass is then withdrawn from the fire, and when cold, lixiviated with water, the solution digested with the insoluble part, filtered and evaporated, when it deposits, on cooling, yellow crystals; which by a second solution and crystallization become quite pure.

The essential points of this process are, first, the presence of as much nitrogen as possible in the animal matter: hence, fresh, dried, uncalcined animal matter is far preferable to animal charcoal. Secondly, the presence of metallic iron, or sulphide of iron: the former is either directly derived from the vessels, which are rapidly corroded, or added as filings; the latter is formed from the iron of the vessels by the action of bisulphide of potassium, which arises from the decomposition, by charcoal at a red-heat, of the sulphate of potash contained in the potashes or pearlash; hence, pure carbonate of potash is not adapted to this process. Thirdly, the exclusion of the air as far as possible, in order to prevent the oxidation and destruction of the cyanide of potassium formed.

The explanation of the process is very simple and beautiful, and we are indebted for it to the researches of Liebig. When animal matter is heated along with potash, cyanogen is formed, and com-

binning with the potassium, (set free at the same time by the action of carbon on potash) produces cyanide of potassium, a salt which is not decomposed by a red-heat in closed vessels. At the same time, metallic iron and sulphide of iron are present in the mixture, but not a trace of the ferrocyanide, previous to the action of water, for the very obvious reason, that the ferrocyanide is decomposed by a red-heat into cyanide of potassium and carbide of iron, nitrogen being disengaged.

If the cooled mass be now digested in water, the cyanide of potassium dissolves either the metallic iron with disengagement of hydrogen, or the sulphide of iron, and the filtered liquid now contains the ferrocyanide.

Direct experiments have shown that cyanide of potassium dissolves either iron, oxide of iron, or sulphide of iron, producing the ferrocyanide, $3 \text{ K Cy} + \text{Fe} + \text{H O} = (2 \text{ K Cy} + \text{Fe Cy}) + \text{K O} + \text{H}$; or, $3 \text{ K Cy} + \text{Fe S} = (2 \text{ K Cy} + \text{Fe Cy}) + \text{K S}$. And it has also been shown by Liebig that if the fused mass be lixiviated with alcohol, the residue, when treated with water, yields no ferrocyanide, while the alcohol contains none, but only cyanide of potassium.

Taking these facts into consideration, perhaps the best method would be to use pure carbonate of potash, free from sulphate, by which means no sulphide of potassium would be formed, and the iron vessels would not suffer as they now do. The cyanide of potassium, being dissolved in water and filtered, should then be placed in contact with iron turnings, in flat open vessels, when the third part of the potassium being oxidized by the air, the iron is rapidly dissolved, and a quantity of ferrocyanide obtained equal to that indicated by the cyanide of potassium present.

The ferrocyanide of potassium forms large honey-yellow, transparent, flat, quadrangular prisms, derived from a rhombic octahedron. It is very soluble in water, and forms precipitates in almost all metallic solutions, many of which are characteristic. Thus with solutions of zinc and lead it gives a white precipitate, with those of copper a chesnut-brown, with those of peroxide of iron a deep blue, with protoxide of iron a pale blue, with those of barium and calcium whitish-yellow crystalline precipitates. The lead precipitate is Cfy, Pb_2 ; that of copper, Cfy, Cu_2 ; those of barium and calcium, $\text{Cfy } \left\{ \begin{smallmatrix} \text{K} \\ \text{Ba} \end{smallmatrix} \right.$ and $\text{Cfy } \left\{ \begin{smallmatrix} \text{K} \\ \text{Ca} \end{smallmatrix} \right.$; and that of zinc, $2 \text{ Cfy} + \left\{ \begin{smallmatrix} \text{Zn} \\ \text{K} \end{smallmatrix} \right.$

$+ 6 \text{ aq} = \text{Cfy, Zn}_2 + \text{Cfy } \left\{ \begin{smallmatrix} \text{Zn} \\ \text{K} \end{smallmatrix} \right. + 6 \text{ aq}$. That of protoxide of iron is $2 \text{ Cfy } \left\{ \begin{smallmatrix} \text{Fe} \\ \text{K} \end{smallmatrix} \right. = \text{Cfy, Fe}_2 + \text{Cfy } \left\{ \begin{smallmatrix} \text{Fe} \\ \text{K} \end{smallmatrix} \right.$ All of these formulæ are easily referred to the general formula of the ferrocyanides, Cfy, M_2 .

Ferrocyanide of Iron.—But the most remarkable of all these compounds, is that formed with persalts of iron, namely, Prussian

blus. It is produced when ferrocyanide of potassium comes in contact with perchloride, or any salt of peroxide of iron. Now as ferrocyanogen is a bibasic radical, 1 eq. of it corresponds with 2 eq. of potassium, hydrogen, oxygen, chlorine, &c.; and as perchloride of iron, $\text{Fe}_2 \text{Cl}_2$, contains 3 eq. of chlorine, $1\frac{1}{2}$ eq. of ferrocyanide of potassium will be required to decompose 1 eq. of it, or, to avoid fractions, 3 eq. of ferrocyanide, $\text{Cfy, K}_2 = 3 \text{ Cfy, K}_2$, are required for 2 eq. perchloride of iron, $2 \text{ Fe}_2 \text{Cl}_2 = \text{Fe}_4 \text{Cl}_4$. The result is, $\text{Cfy, K}_2 + \text{Fe}_2 \text{Cl}_2 = 6 \text{ K Cl} + \text{Cfy, Fe}_2$; and this last is the true formula of Prussian blue, although, from its tendency to combine both with ferrocyanide of potassium and with oxide of iron, its analysis offers great difficulties. The formula Cfy, Fe_2 , or $\text{Fe}_2 \text{Cfy}_2$, shows that Prussian blue corresponds to peroxide and perchloride (sesquioxide and sesquichloride) of iron, $\text{Fe}_2 \text{O}_2$ and $\text{Fe}_2 \text{Cl}_2$, for Cfy being bibasic is equivalent to Cl_2 or O_2 , and consequently $\text{Fe}_2 \text{Cfy}_2$ is equivalent to $\text{Fe}_2 \text{Cl}_2$ or $\text{Fe}_2 \text{O}_2$, that is to $2 \text{ Fe}_2 \text{Cl}_2$ and $2 \text{ Fe}_2 \text{O}_2$. It must be admitted to be a very strong argument in favor of the existence of ferrocyanogen, as a bibasic radical, according to the theory of Liebig, that Prussian blue, in all other theories, the most complex and anomalous compound in the whole range of chemistry, becomes quite normal and one of a series.

Ferrocyanide of potassium is employed to yield cyanogen and all its compounds.* We have already seen how cyanogen, hydrocyanic acid, cyanide of potassium, cyanate of potash, urea, cyanic and cyanuric acids, and ferrocyanic acids are obtained from it. Cyanide of potassium, for testing, and to be used as a flux and in analysis, is best prepared, according to Liebig, by heating 8 parts of the dry ferrocyanide with 3 of pure carbonate of potash in an iron vessel till the fused mass is colorless. It is then poured off from the sponge of reduced iron, and kept in well-stoppered bottles. The reaction is as follows, (representing the ferrocyanide, for convenience, as a double cyanide of iron and potassium): $2 (\text{Fe Cy, 2 K Cy}) + 2 (\text{K O, C O}_2) = \text{Fe}_2 + 5 \text{ K Cy} + \text{K O, Cy O} + 2 \text{ C O}_2$.

* The new gunpowder which has been noticed in most of the journals of the day, is a mixture of ferrocyanide of potassium, white sugar, and chlorate of potassa. The best proportions in which they should be mixed, according to M. AUGENDRE, (*Comptes Rendus*), are:

Pulverized ferrocyanide of potassium,	1 part,
" white sugar,	1 part,
" chlorate of potassa,	2 parts.

The ingredients are pulverized separately and then mixed. This powder possesses greater force than gunpowder, but it will not be likely to come into general use, as it exerts an erosive effect upon iron, and is greatly liable to spontaneous inflammation. All mixtures into which chlorate of potassa enters are dangerous, from the great tendency this salt has to ignite with combustible materials. The above powder, therefore, although highly recommended by M. AUGENDRE, is dangerous, and should not be manufactured or kept in large quantities.

Hence the resulting salt contains 1 eq. cyanate of potash to 5 eq. cyanide of potassium. This very useful preparation, known as Liebig's cyanide of potassium, is not quite pure, containing cyanate of potash: but this does not interfere with its use.

Another very remarkable compound is produced by the action of a current of chlorine gas on the solution of ferrocyanide, if transmitted until the solution ceases to produce Prussian blue with perchloride of iron, yielding only a brownish-green color, but no precipitate. The liquid now gives, on evaporation, beautiful deep hyacinth-red crystals of a new salt, the ferridecyanide of potassium, discovered by Gmelin. This salt contains a new radical, ferridcyanogen.

V. FERRIDCYANOGEN. $Cy, Fe_3 = Cfdy = 211.74$.

This radical has not yet been isolated. It is formed by the coalescence of 2 eq. of ferrocyanogen, and is tribasic. It forms an acid with hydrogen, and salts with metals.

Ferridecyanic Acid, $(Cy, Fe_3) + H_3 = (3 Cfy + H_3) = Cfdy, H_3 = 214.74$.

This acid is obtained from the lead salt $Cfdy, Pb_3$, by the action of sulphuric acid. It is soluble in water, and by the action of sulphuretted hydrogen is converted into ferrocyanic acid: $2 Cfy, H_3 + H_2 S = 2 (Cfy, H_3) + S$. With bases it forms salts; as with potash the ferridecyanide of potassium.

Ferridecyanide of Potassium. SYN. *Red Prussiate of Potash.*— Its preparation has been described above. Its formula is $2 Cfy + K_3 = Cfdy, K_3$; and it is quite anhydrous. Like the yellow prussiate, it forms precipitates with most metallic solutions, many of which are characteristic. With salts of peroxide or with perchloride of iron, it only strikes a brown or green color, but with protochloride or salts of protoxide, it forms Prussian blue. As the radical is tribasic, 1 eq. of it ought to be equivalent to 3 eq. of oxygen, chlorine, &c.; and if we suppose the potassium in the ferridecyanide replaced by its equivalent of iron, we should have $Cfdy, Fe_3 = Fe_3, Cy_3$; for $K_3, Cfy_3 + 3 Fe O = Fe_3, Cfy_3 + 3 K O$; and $Fe_3, Cfy_3 = Fe_3, Cy_3$. But, instead of this compound, there is formed Prussian blue, the same we have above described as being formed by the action of yellow prussiate or peroxide of iron.

In fact, when the red prussiate is added to a solution of a salt of protoxide, or to protochloride of iron, yellow prussiate is formed along with Prussian blue and a salt of potash. Bearing in mind, as in all the above explanations, that 1 eq. ferridecyanogen $Cfdy$ is equal to 2 eq. ferrocyanogen Cfy , and that, consequently, the red prussiate, $Cfdy, K_3$, may be equally well represented as $2 Cfy, K_3$, then we have $2 (2 Cfy, K_3) + 4 (Fe O, S O_3) = (3 Cfy + Fe_3) + (Cfy, K_3) + 4 (K O, S O_3)$.

The ferridcyanide of potassium may be viewed as ferrocyanide of potassium, *plus* a certain amount of ferrocyanogen: $2 \text{ (Cfdy, K}_3\text{)} = 3 \text{ (Cfy, K}_3\text{)} + \text{Cfy}$.

With salts of lead, ferridcyanide of potassium forms the ferridcyanide of lead, Cfdy, Pb₃.

VI. COBALTOCYANOGEN. $\text{Cy, Co}_3 = \text{Cky} = 216.52^*$

Not yet isolated, but known in combination with hydrogen, potassium, &c. It is analogous to ferridcyanogen in constitution, and like it, is tribasic.

Cobaltocyanic Acid, Cky H₃ = 219.52. — Obtained by the action of sulphuric acid on cobaltocyanide of lead, Cky, Pb₃. It forms silky filaments, which are deliquescent and strongly acid.

Cobaltocyanide of Potassium, Cky, K. — Is obtained by acting on a salt of oxide of cobalt with solution of cyanide of potassium and hydrocyanic acid, when hydrogen is given off and the new salt is obtained in crystals. The protocyanide of cobalt, precipitated on the first addition of cyanide of potassium, redissolves in an excess of that salt, forming a compound, $2 \text{ Co Cy} + \text{K Cy}$, or $2 \text{ Co Cy} + 3 \text{ K Cy}$. At all events, there is enough of cyanide of potassium present to form the latter compound. The hydrocyanic acid, being now added, yields 1 eq. of cyanogen, converting the 2 eq. of protocyanide into 1 eq. of sesquicyanide of cobalt, while hydrogen is given off: $2 \text{ Co Cy} + \text{H Cy} = \text{Co}_3 \text{ Cy}_3 + \text{H}$. Lastly, the sesquicyanide $\text{Co}_3 \text{ Cy}_3$, with the 3 eq. of cyanide of potassium, 3 K Cy , produces the cobaltocyanide of potassium, $\text{Cy, Co}_3 + \text{K}_3 = \text{Cky, K}_3$. The crystals are isomorphous with those of the red prussiate of potash; they are yellow, soluble; their solution is not altered by acids, and gives, in solution of protoxide of cobalt, a beautiful rose-colored precipitate, analogous probably to Prussian blue; possibly, however, it may be Cky, Co₃. It precipitates many other metallic solutions, such as those of lead and silver.

Cobaltocyanide of potassium is a singularly permanent salt, resisting the action of the strongest acids; which is, in itself, a sufficient proof that it cannot contain cyanide of potassium as such. With the salts of nickel it forms a green precipitate, Cky, Ni₃, which is insoluble in boiling dilute acids. This property has been applied by Liebig to the separation of cobalt from nickel in analysis. All other metals being removed, an excess of potash is first added, and then hydrocyanic acid till the precipitate at first formed is dissolved, and the whole is then boiled. Hydrochloric acid is now added, and if no nickel be present, it produces no change, because it has no action on cobaltocyanide of potassium. But if nickel be present (of course by this time as cyanide) it is converted into chloride, and this is instantly precipitated by the

* The better name for this would be Cobaltidcyanogen. — S.

cobaltocyanide of potassium as cobaltocyanide of nickel. Should there be more cobalt than nickel present, the whole nickel is precipitated, and the precipitate, acted on by potash, leaves the nickel as peroxide, while the cobalt is dissolved as cobaltocyanide, and may be determined along with the portion not precipitated for want of nickel. If, on the other hand, there be more nickel than cobalt, all the cobalt is contained in the green precipitate of cobaltocyanide of nickel, and may be dissolved by potash, and its quantity determined, while the nickel left by the potash as peroxide may be added to that left in the liquid for want of cobalt. Such is an outline of this very beautiful and refined method, which gives most accurate results.

VII. CHROMOCYANOGEN. $Cy, Cr = Cry$.*

This radical is little known. It is analogous to the two preceding; forming with hydrogen an acid, Cry, H_2 , and with potassium a yellow crystallizable salt, Cry, K_2 , which precipitates metallic solutions.

VIII. PLATINOCYANOGEN. $Cy, Pt = Cpy = 151.38$.

This radical is not known in the separate state. It forms with hydrogen a crystallizable acid of a gold or copper color and metallic lustre, Cpy, H_2 , which is very soluble and deliquescent. This acid is powerful, decomposes the carbonates, and produces platino-cyanides. Platinocyanide of potassium, Cpy, K_2 , is easily obtained by heating spongy platinum, or, still better, finely divided platinum black to low redness with twice its weight of dried ferrocyanide of potassium, and lixiviating with water; or by dissolving protochloride of platinum in hot solution of cyanide of potassium. It forms crystals yellow and metallic by transmitted, blue by reflected light. By the action of this salt on protonitrate of mercury, a cobalt-blue precipitate is formed, which, when heated in the fluid, becomes white, and is then pure platinocyanide of mercury, $Cpy, Hg (?)$. This salt, acted on by sulphuretted hydrogen, yields the platino-cyanic acid. A solution of platinocyanide of potassium acted on by chlorine, yields beautiful copper-like crystals of a new salt, which is either a double cyanide, $2 K Cy + Pt_2 Cy_2 + 5 H O$; or the potassium salt of a new radical, $Pt_2 Cy, K_2 + 5 H O$. — (*Knop*.)

The platinocyanides of barium, strontium, and calcium, are easily obtained by the action of platino-cyanic acid on these bases, and crystallize readily in beautiful greenish-yellow color, or in some cases green and red with metallic lustre.

IX. IRIDIOCYANOGEN. $Cy, Ir = Ciy$.

This radical has not been isolated. It forms, with hydrogen, iridiocyanic acid, Cy, Ir, H_2 , which is obtained by the action of sulphuretted hydrogen on iridiocyanide of lead, Cy, Ir, Pb_2 .

* Chromidecyanogen. — S.

Iridiocyanide of Potassium, Cy, Ir, K_3 —Is obtained by the action of protochloride of iridium on cyanide of potassium. It forms colorless crystals; its solution gives, with salts of peroxide of iron, a deep indigo color.

There appears to be a series of similar compounds formed by cyanide of palladium. The palladiocyanide of potassium corresponds to the platinocyanide, and its formula is Cy, Pd, K .

There is also reason to believe that manganese forms a manganocyanogen, corresponding to ferridcyanogen, $\text{Cy, Mn}_2 = \text{Cmy}$. The manganocyanide of potassium is probably $\text{Cy, Mn}_2 + \text{K}_3 = \text{Cmy, K}_3$.

From what has been stated in the preceding pages, it will be seen that cyanogen has a very great tendency to form cyanides containing 2 or 3 metals, and likewise cyanides containing one of these metals and hydrogen in the place of the other. As these latter compounds are very powerful acids, we are naturally led to consider them as hydrogen acids, in which the hydrogen is combined with radicals. This view has been adopted above, and we have seen reason to admit the following radicals:

Platinocyanogen,	$\text{Cpy} = \text{Cy, Pt}$
Palladiocyanogen,	$\text{Cpdy} = \text{Cy, Pd}$
Ferrocyanogen,	$\text{Cfy} = \text{Cy, Fe}$
Iridiocyanogen,	$\text{Ciy} = \text{Cy, Ir}$
Ferridecyanogen,	$= \text{Cfdy} = \text{Cy, Fe}_2$
Cobaltidecyanogen,	$= \text{Cky} = \text{Cy, Co}_2$
Chromidecyanogen,	$= \text{Cry} = \text{Cy, Cr}_2$
Manganidecyanogen,	$= \text{Cmy} = \text{Cy, Mn}_2$

It will be observed that there are three different formulæ among these radicals, namely, Cy, M ; Cy, M_2 ; and Cy, M_3 ; the first monobasic, the second bibasic, the third tribasic. No other view can at present be given of these compounds, of their acids, and of their salts, which is at once so satisfactory, so consistent, and so advantageous for the learner, as being adapted to assist the memory. It is true that the acids may be viewed as compounds of cyanide of a metal with cyanide of hydrogen, (hydrocyanic acid), and their salts as compounds of two metallic cyanides. Thus, ferrocyanic acid, $\text{Cy, Fe} + \text{H}_2$, may be said to be $2 \text{ H Cy} + \text{Fe Cy}$, and ferrocyanide of potassium, $2 \text{ K Cy} + \text{Fe Cy}$. Again, ferridcyanic acid may be $3 \text{ H Cy} + \text{Fe}_2 \text{ Cy}$, and its potassium salt $3 \text{ K Cy} + \text{Fe}_2 \text{ Cy}$; while platinocyanic acid and its potassium salt may be $\text{H Cy} + \text{Pt Cy}$ and $\text{K Cy} + \text{Pt Cy}$.

But the strong acid properties and inert nature of these acids, and the remarkable permanence, both of the acids and of the salts, are entirely inconsistent with the presence of so weak an acid and so frightful a poison as hydrocyanic acid, or of bodies so easily decomposed as hydrocyanic acid and cyanide of potassium.

Besides, there are numerous double cyanides, such as K Cy, Zn Cy; K Cy, Cd Cy; K Cy Cu, Cy, &c. &c. &c., which act as such; being easily decomposed, and exhibiting no indications of containing radicals like those above described. We shall therefore not dwell on any other view, and merely allude here to the true double cyanides, as belonging more to the history of the metals, and less to that of the organic radicals.

PARACYANOGEN.

As an appendix to the metallic cyanides, we may here mention this compound, which is left behind as a dark brown powder, when cyanide of mercury is heated in a retort. As cyanogen and mercury alone are given off, we should expect the salt to be dissipated by heat entirely; but this not being the case, it is evident that the residue, if it contain no mercury, must have the same composition as cyanogen, and be, in short, an isomeric modification of it—a solid cyanogen. Again, when cyanide of silver is heated, it gives off part of its cyanogen; it then glows, and, if soon removed from the fire, yields a peculiar residue, which is only partly dissolved by nitric acid. The insoluble residue appears to contain silver and cyanogen in the proportion Ag Cy₂, and it is probable that the cyanogen here is in the solid modification, of which 1 eq. is supposed to be formed by 3 eq. of cyanogen.

Whether, therefore, we admit paracyanogen as a separate radical or not, the two residues just mentioned contain carbon and nitrogen in the proportions to form cyanogen. It is also possible that some such compound may exist in cast iron and steel, which appear to contain nitrogen as well as carbon.

In treating of mellone, we shall see that doubts may be entertained of the existence of paracyanogen, and that the proportions of carbonic acid and nitrogen gasses obtained in analyzing the supposed paracyanogen may be derived from a mixture of mellone and carbon.

CYANOGEN AND SULPHUR.

X. SULPHOCYANOGEN. Cy S₂ = Csy.

Syn. Bisulphide of Cyanogen.—When ferrocyanide of potassium is heated with sulphur, there is formed a new salt, the formula of which is Cy S₂ + K. This is sulphocyanide of potassium, which appears to contain the radical Cy S₂, or Csy. We cannot say that this radical is known in the free state, but by the action of chlorine on sulphocyanide of potassium there is formed a bright orange powder, which contains sulphocyanogen, mixed with some other bodies. Like the preceding radicals, sulphocyanogen, with hydrogen, forms a peculiar acid, the sulphocyanic or hydrosulphocyanic acid.

Hydrosulphocyanic Acid, Cy S₂, H = Csy H—Is obtained by passing sulphuretted hydrogen gas through sulphocyanide of lead,

Csy, Pb, suspended in water. The solution thus formed is highly acid, and has the odor of acetic acid. It strikes a blood-red color with salts of peroxide of iron, and this property is found in all soluble sulphocyanides. The formula of this acid corresponds to that of cyanic acid, $\text{Cy O}_2, \text{H}$; and it may be viewed as cyanic acid, the oxygen of which has been replaced by sulphur. With metallic oxides, it forms the sulphocyanides of the metals, $\text{Cy S}_2, \text{H} + \text{M O} = \text{Cy S}_2, \text{M} + \text{H O}$.

Sulphocyanide of Potassium, $\text{Cy S}_2, \text{K} = \text{Csy, K}$. — The best process for obtaining this salt is to melt at a gentle heat (only raised at the end to low redness) 46 parts of dried ferrocyanide of potassium, 32 of sulphur, and 17 of pure carbonate of potash. The mass when cold is boiled with water, and the solution, being filtered and evaporated, deposits striated prismatic crystals of the salt, very similar in appearance, and in taste also, to nitre.

If not quite pure, it is purified by solution in alcohol and recrystallization. In this process, the whole cyanogen of the ferrocyanide is first converted into cyanide of potassium, and then, by the taking up of sulphur, into sulphocyanide; while the iron is converted into sulphide. As 1 eq. ferrocyanide contains 3 eq. of cyanogen and 2 of potassium, 1 eq. of carbonate of potash is added, and the 3 eq. of cyanide of potassium thus obtained take up 6 eq. of sulphur to form the new salt: $3 \text{ K Cy} + \text{S}_6 = 3 (\text{Cy S}_2, \text{K})$.

Sulphocyanide of potassium causes precipitates in some metallic solutions, but as many metallic sulphocyanides are soluble, the greater number of metals are not precipitated by this salt. With salts of peroxide of iron it strikes an intense blood-red color, but causes no precipitate. With acetate of lead it gives yellow crystals, and with subacetate a white precipitate, and with salts of suboxide of copper also an insoluble white subsulphocyanide of copper. Sulphocyanide of silver is precipitated as a curdy white solid, when sulphocyanide of potassium is added to nitrate of silver. The other sulphocyanides are soluble.

When sulphocyanic acid is set free from its salts, by diluted acids, and exposed to heat, it is resolved, with the aid of the elements of water, into carbonic acid, bisulphide of carbon, and ammonia: $\text{C}_2 \text{ N S}_2, \text{H} + \text{H}_2 \text{ O}_2 = \left. \begin{matrix} \text{C S}_2 \\ \text{C O}_2 \end{matrix} \right\} + \text{N H}_3$. Compare this with the spontaneous decomposition of cyanic acid when set free from its salts: $\text{C}_2 \text{ N O}_2, \text{H} + \text{H}_2 \text{ O}_2 = \left. \begin{matrix} \text{C O}_2 \\ \text{C O}_2 \end{matrix} \right\} + \text{N H}_3$.

This shows that the view which considers sulphocyanic acid as cyanic acid, the oxygen of which has been replaced by sulphur, is confirmed by the similarity in the decomposition of these two acids; which, in this point of view, may be said to belong to the same type.

When sulphocyanide of potassium is mixed with 6 or 8 volumes of strong hydrochloric acid, hydrocyanic acid is given off, and a new crystalline acid is deposited, which contains more sulphur, and may be called (hydro) persulphocyanic acid: $3 (\text{Cy S}_2 \text{H})$, that is, 3 eq. of sulphocyanic acid lose Cy H , 1 eq. of hydrocyanic acid, and there remain 2 eq. of the compound $\text{Cy S}_2, \text{H}$, or persulphocyanic acid. The formula of its salts is $\text{Cy S}_2, \text{M}$. When the acid is dissolved in ammonia, it soon deposits sulphur, and the liquid retains a new compound $\text{Cy}_2 \text{S}_2, \text{H}_2 (= 2 \text{Cy S}_2, \text{H} - \text{S})$ combined with ammonia: on adding an acid, persulphocyanic is reproduced and deposited, while sulphocyanic acid remains in the solution: $\text{Cy}_2 \text{S}_2, \text{H}_2 = \begin{cases} \text{Cy S}_2, \text{H} \\ \text{Cy S}_2, \text{H} \end{cases}$.

When solution of sulphocyanide of potassium is acted on by chlorine or by nitric acid, a bright orange-yellow powder is deposited which was long supposed to be sulphocyanogen; but it now appears to be a compound or mixture of sulphocyanogen, sulphocyanic acid and water, in the proportions $3 \text{Cy S}_2 + \text{Cy S}_2, \text{H} + \text{H O} = \text{C}_4 \text{N}_4 \text{S}_6 + (\text{C}_2 \text{N S}_2, \text{H}) + \text{H O} = \text{C}_4 \text{N}_4 \text{S}_6 \text{H}_2 \text{O}$. This yellow compound undergoes a very remarkable change when heated: it gives off bisulphide of carbon, sulphur, and a little persulphocyanic acid, and there is left in the retort a grayish-yellow powder, containing no sulphur, oxygen, or hydrogen, and not decomposed by a low red-heat. By a strong red-heat it is dissipated, yielding a mixture of 3 vol. cyanogen to 1 vol. nitrogen.

This residue may be viewed as a cyanide of nitrogen, $\text{N Cy}_2 = \text{C}_2 \text{N}_4$, and as it plays the part of a radical, analogous to cyanogen, it is called mellone, and has the symbol Me . Its production from sulphocyanogen is easily explained: $4 (\text{C}_2 \text{N S}_2) = 2 \text{C S}_2 + \text{S}_4 + \text{C}_2 \text{N}_4$. If the orange-yellow compound which yields it be thrown into melted sulphocyanide of potassium the mellone actually seizes the potassium, expelling the sulphocyanogen, which is resolved into bisulphide of carbon, sulphur, cyanogen, and nitrogen, all of which escape with effervescence. This is because mellone is not only a powerful radical, but also capable of resisting a strong heat.

XI. MELLONE. $\text{Me} = \text{C}_2 \text{N}_4 = 92.94$.

The preparation of this radical by the action of heat on impure sulphocyanogen, has been described above. It may also be obtained by heating to low redness the sulphocyanide of ammonium, as will be explained below. It appears as a grayish-yellow powder, which is capable of combining directly with potassium when heated with it, and of decomposing sulphocyanide of potassium, as before mentioned. In both cases it forms a fusible, soluble, crystallizable salt, mellonide of potassium. When to the solution of this salt an acid is added, it causes a white gelatinous precipitate,

which is an acid, sparingly soluble in water, the hydromellonic acid.

Hydromellonic Acid, $\text{Me H} = \text{C}_6 \text{N}_4, \text{H}$ —Is best formed by mixing a hot solution of mellonide of potassium with strong hydrochloric acid, when, on cooling, hydromellonic acid is deposited as a snow-white powder. It is somewhat soluble in hot water, sparingly so in cold; it is a strong acid, and with acetate of potash produces mellonide of potassium, displacing the acetic acid. If, however, a saturated hot solution of the mellonide be mixed with acetic acid, half the potash is removed, and on cooling, crystals of an acid salt are deposited, which, in the case of a hydrogen acid, is very unusual. It is possible, however, that hydromellonic acid may be bibasic, which would account for the fact of its forming an acid salt. This acid is very remarkable for its power of resisting heat, as it requires a full red-heat to decompose and dissipate it.

Mellonide of Potassium, $\text{Me, K} = \text{C}_6 \text{N}_4, \text{K}$ —Occurs as an accidental product in the making of sulphocyanide of potassium. It is best obtained by fusing at a low red-heat, in a covered iron crucible, dried ferrocyanide of potassium, with about half its weight of sulphur, and adding, toward the end of the fusion, about 5 per cent. of dried carbonate of potash. The cooled mass is boiled with water, and the filtered solution concentrated, till, on cooling, it forms a semi-solid mass of minute needles, which are purified from sulphocyanide by washing with alcohol, in which the mellonide is insoluble. The mellonide may also be obtained by adding mellone to fused sulphocyanide of potassium, when, by the decomposition of the sulphocyanogen, an additional quantity of mellone is formed. In the first process also, a portion of mellone is formed by the action of heat on the sulphocyanide of iron, produced at the commencement of the fusion; and this mellone acts, as in the second process, on the sulphocyanide of potassium, giving rise, in so doing, to an additional amount of mellone: hence the advantage of adding some carbonate of potash to prevent any loss of mellone. Finally, mellonide of potassium may also be prepared by adding 2 parts of dry subsulphocyanide of copper to 3 of fused sulphocyanide of potassium.

Mellonide of potassium is soluble in water, insoluble in alcohol. It has a bitter taste, and its crystals contain 5 eq. of water, of which 4 eq. are expelled at 212° . When acted on by hydrochloric acid, it yields hydromellonic acid; when by acetic acid, it gives the acid salt above-mentioned. By the action of mellonide of potassium on the salts of baryta, strontia, lime, or magnesia, the mellonides of barium, &c., are obtained as sparingly soluble salts, which crystallize in fine needles.

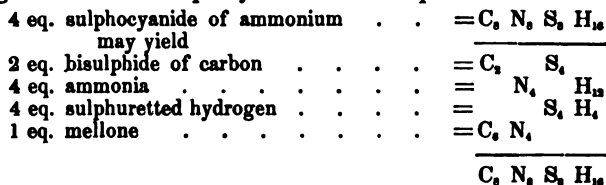
By boiling mellonide of potassium with excess of potash, ammonia is given off, and a new salt is formed. This, decomposed by

acetic acid, yields a white crystalline precipitate, containing no potash, probably a new acid. When dilute solution of mellonide of potassium is acted on by strong hydrochloric acid, and boiled till the hydromellonic acid is redissolved, the liquid, on cooling, deposits cyanuric acid, and contains sal ammoniac. Hydromellonic acid $Cy, N H$, with 3 eq. of water $H_2 O$, and 1 eq. oxygen, yields dry cyanuric acid, Cy, O_3 , and oxide of ammonium, $N H_4 O$. The equivalent of oxygen is probably derived from the atmosphere; but this decomposition, as well as the preceding, requires minute investigation.

PRODUCTS OF THE DISTILLATION OF SULPHOCYANIDE OF AMMONIUM.

As an appendix to sulphocyanogen and its derivative mellone, we may consider the remarkable results of the action of heat on sulphocyanide of ammonium, $N H_4, C, N S_2$.

When this salt is heated in a retort, there are given off as gases or vapors, bisulphide of carbon, ammonia, and sulphuretted hydrogen, the two latter partly combined as sulphide of ammonium:



Such is, in fact, the result of the action of a strong heat on the salt, mellone alone remaining in the retort. But if a more moderate heat be employed, a gray residue is left, containing the elements of mellone with those of ammonia. If this crude residue be dissolved in boiling potash, and the solution quickly filtered, there is deposited, on cooling, a heavy white powder, which is the chief product of the distillation of the sulphocyanide, in a state of purity. It has been called Melam, and its formula is $C_{12} N_{11} H_2 = 2 C_6 N_4 + 3 N H_3$, or 2 eq. mellone and 3 eq. ammonia.

When the crude melam is acted on by oil of vitriol it dissolves with the aid of a gentle heat, and if water be added, and the whole boiled till the addition of carbonate of ammonia causes no further precipitate, the liquid, on cooling, deposits a large quantity of cyanuric acid, and is found to contain sulphate of ammonia. Now, as mellone, by the action of acids or alkalies, yields cyanuric acid and ammonia, it is easy to see that melam should do the same, $C_{12} N_{11} H_2$; that is, melam is equal to 2 eq. mellone $C_6 N_4$, and 3 eq. ammonia $N H_3$; and if we represent mellone by Cy, N , melam will be $2 Cy, N + 3 N H_3$. Now let us add 12 eq. of water, and $2 Cy, N + H_{12} O_{12} = 2 (Cy, O_6, H_2) + 2 N H_3$, and adding the 3 eq. of ammonia already present in melam, we have 2 eq. hydrated cyanuric acid, $2 (Cy, O_6, H_2)$, and 5 eq.

ammonia, 5 N H₃, as the final results from 1 eq. melam and 19 eq. water, under the influence of acids and heat.

When melam is acted on by boiling with potash, a series of new compounds is obtained. The first is melamine, which is deposited in crystals when the alkaline solution cools. Melamine contains no oxygen, but is an artificial organic base, neutralizing acids, and forming salts. Its formula is C₃ N₃ H₃ = C₃ N₃ + N₃ H₃; that is, it contains the elements of 1 eq. mellone, and 2 eq. ammonia.

The second new body is obtained as a white powder, when the alkaline solution which has deposited melamine, is supersaturated with acetic acid. It is called ammeline, and is also a base, although weaker than melamine. Its formula is C₆ N₄ H₅ O₂ = C₆ N₄ + N H₃ + 2 H O, or 1 eq. mellone, 1 eq. ammonia, and 2 eq. water. It forms a crystallizable salt with nitric acid.

It may here be observed, that melam, C₁₂ N₁₁ H₉, with 2 eq. water, H₂ O₂, contains the elements of 1 eq. melamine, C₃ N₃ H₃, and 1 eq. ammeline, C₆ N₄ H₅ O₂.

When either melamine or ammeline is dissolved in strong sulphuric acid, or melam in nitric acid, and the solution mixed first with two vol. of water, and then with four of alcohol, a white powder is obtained, resembling ammeline, but having the formula C₁₂ N₉ H₅ O₆ = 2 C₆ N₄ + N H₃ + 6 H O, or 2 eq. mellone, 1 eq. ammonia, and 6 eq. water. It is called ammelide, and has rather the characters of an acid than of a base.

Melamine, by the action of hydrochloric acid, aided by heat, is transformed into ammeline, giving off ammonia, while water is taken up: C₃ N₃ H₃ + H₂ O₂ = C₆ N₄ H₅ O₂, and C₃ N₃ H₃ - N H₃ = C₆ N₄ H₅ O₂.

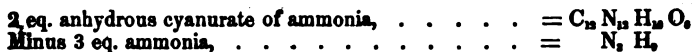
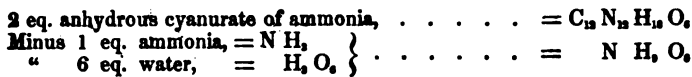
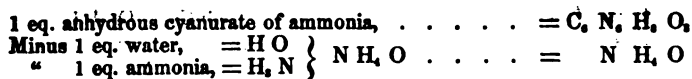
Melam, also, when treated in the same way, yields ammeline and ammonia: C₁₂ N₁₁ H₉ + H₂ O₂ = C₁₂ N₁₁ H₁₃ O₄; and C₁₂ N₁₁ H₁₃ O₄ - N H₃ = C₁₂ N₁₀ H₁₀ O₄ = 2 (C₆ N₄ H₅ O₂).

All these substances may be resolved, by the action of acids, into cyanuric acid and ammonia. It appears that they are all, that is, melam, melamine, and ammeline, first converted into ammelide, and that ammelide is the source of the cyanuric acid and ammonia.

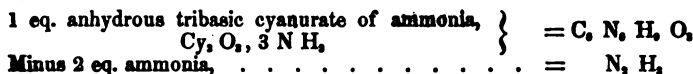
It is obvious that they are all closely related to each other, and to cyanuric acid. That they are also related to mellone is probable, because when heated they leave a yellow residue, which is converted by a stronger heat into cyanogen and nitrogen; which, in short, is mellone. All these compounds may be represented as tribasic cyanurate of ammonia, minus water, or water and ammonia. Thus,

1 eq. anhydrous cyanurate of ammonia, Cy, O₃, 3 N H₃ = C₃ N₃ H₃ O₃,
Minus 3 eq. water, = H₂ O₃

Yields 1 eq. melamine, = C₃ N₃ H₃



When the mass remaining in the retort when urea is heated, and formerly believed to be cyanuric acid or cyanurate of ammonia, is acted on by acids, it yields cyanuric acid, and ammonia is found in the solution; but if it be boiled with water, an insoluble snow-white powder is obtained, which agrees with ammelide in almost all its properties. Its formula, however, is $C_3 N_3 H_3 O_3$, and it may also be derived from cyanurate of ammonia, as follows:—

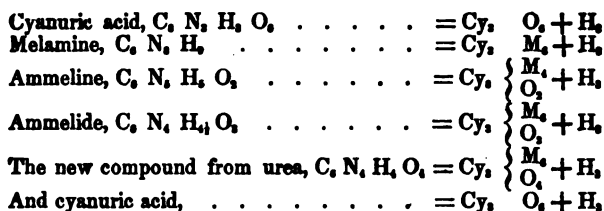


This product, therefore, is intermediate between ammelide and cyanuric acid.

To be transformed into hydrated cyanuric acid, it has only to lose 1 eq. ammonia, and to gain 2 eq. water. Its formation from urea is very easily understood; for 4 eq. urea minus 2 eq. carbonic acid and 4 eq. ammonia, will give this compound:

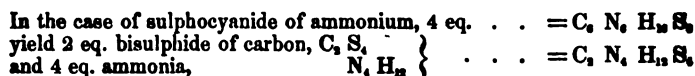
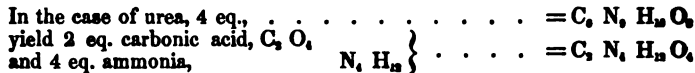


In order to render still more obvious the relation of these compounds, melam excepted, to cyanuric acid and among each other, let us express the hypothetical compound $N H$ by M , M , therefore, standing for $\frac{1}{3}$ eq. $N H$. We then have,



Here we see the change in properties accompanying the gradual substitution of M for O. At one end of the series is melamine, a base, containing no oxygen; at the other, cyanuric acid, a highly oxygenized acid; while ammeline is a weak base, and the remaining two are neutral, or have a tendency, but a very slight one, to acid properties.

Before quitting these compounds, it is proper to point out that as sulphocyanic acid corresponds to cyanic acid, sulphur being substituted for oxygen, so sulphocyanide of ammonium corresponds precisely in the same way to urea; for urea is $C_2 N_2 H_4 O_2$, and sulphocyanide of ammonium is (see above) $C_2 N_2 H_4 S_2$. That this analogy is not imaginary, we have seen in the similarity of the action of heat on both.



The analogy only fails here in the fact, that the elements $C_2 N_2 H_4 S_2$, instead of uniting, as $C_2 N_2 H_4 O_2$ do, to form one compound, are resolved into two, namely, mellone and sulphuretted hydrogen. Of course, the substance from urea may be viewed as a compound of 1 eq. mellone and 4 of water; and it may possibly hereafter be resolved into those substances.

When mellone is boiled with nitric acid a new acid is formed, crystallizing in octahedrons, which, when redissolved in water, form pearly scales. Liebig, who alone has studied it, found its formula and all its reactions exactly like those of cyanuric acid, and called it cyanilic acid: 1 eq. mellone and 6 eq. water, $C_2 N_2 + H_4 O_6$, are equal to 1 eq. cyanilic (or cyanuric) acid, and 1 eq. ammonia ($C_2 N_2 O_6, H_2$) + $N H_3$. Further experiments are required to establish cyanilic acid as an independent acid.

Sulphomellone. Hydrosulphomellonic Acid.

According to the researches of Jamieson, which have reached me while this sheet was in proof, the orange-yellow powder, commonly called sulphocyanogen, and which, at p. 319, is said to contain 3 eq. of bisulphide of cyanogen, 1 eq. hydrosulphocyanic acid, and 1 eq. water, really consists of the elements of 1 eq. of each of these three substances, $\text{Cy S}_2 + \text{Cy S}_2, \text{H} + \text{H O} = \text{C}_4 \text{N}_4 \text{H}_4 \text{C S}_4$, how arranged we know not.

When dissolved to saturation in hydrosulphide of sulphide of potassium, K S, H S , the elements of 4 eq. sulphocyanogen, $4 \text{ Cy S}_2 = \text{C}_8 \text{N}_8 \text{S}_8$, along with 4 eq. of K S, H S , give rise to 7 eq. sulphuretted hydrogen, 7 H S ; 1 eq. pentasulphide of potassium, K S_5 ; 2 eq. carbonate of potash, $2 (\text{K O, C O}_2)$ and 1 eq. sulphomellonide of potassium, $\text{C}_4 \text{N}_4 \text{H}_4 \text{S}_4, \text{K}$.

When this salt is decomposed by an acid, as hydrochloric acid, a simple exchange takes place. $\text{C}_4 \text{N}_4 \text{H}_4 \text{S}_4, \text{K} + \text{H Cl} = \text{K Cl} + \text{C}_4 \text{N}_4 \text{H}_4 \text{S}_4, \text{H}$. The latter formula represents the hydrosulphomellonic acid, which is a sparingly soluble white crystalline powder. It combines readily with the alcalies, and decomposes the carbonates of the alkaline earths when boiled with them. All the hydromellonides of the metals of the alcalies and alkaline earths are soluble and crystallize beautifully. The general formula for the anhydrous salts is $\text{C}_4 \text{N}_4 \text{H}_4 \text{S}_4, \text{M}$; but the crystallized salts contain from 2 to 6 eq. of water besides. The silver salt is anhydrous. The supposed radical of this acid, and of its salts, is not yet known in a separate state; but when the sulphomellonide of potassium is acted on by chlorine, there is separated a white powder, which seems to be sulphomellone, although Jamieson has not yet had time to ascertain that point. But the acid and its salts are rendered very simple by assuming the existence of this radical, which agrees with all the facts yet known, and makes the sulphomellonides analogous in composition, as they are in their relations, in their origin, and in their properties, to chlorides, bromides, iodides, fluorides, cyanides, and mellonides.

Having now concluded our sketch of the compounds derived from that of sulphur and cyanogen, it only remains to mention that cyanogen forms one or two compounds with sulphuretted hydrogen, and that sulphocyanic acid forms a compound with the same gas. These compounds, however, are as yet too little known to permit of their being clearly laid down.

Cyanogen does not form any compound of importance with phosphorus or the remaining metalloids. But there is a very interesting and important series of compounds, in which we may conceive, with some probability, a radical to exist, formed of the elements of cyanogen and those of oxalyle (see page 287) or carbonic oxide, $\text{C}_2 \text{O}_2$. This is the series of compounds derived from uric acid, and consequently closely connected with urea, which we

have seen to be derived from cyanate of ammonia, and, through cyanic acid, from cyanuric acid, which connects it again with melone, melam, and sulphocyanogen.

We shall first briefly describe the uric acid itself, as the starting point of an extensive series of products. The radical supposed to exist in these compounds will be better understood if described after we have become acquainted with them.

CYANOGEN WITH CARBONIC OXIDE.

XII. URYLE.

URIC ACID. $C_{12}N_4H_2O_6 = C_{12}N_4H_2O_5 + H O$; or, $C_{12}N_4H_2O_5, 2 H O$; or, $C_{12}N_4H O_5, H O$ (Bensch).

SYN. Uric Acid — Lithic Acid — Occurs in small quantity in the healthy urine of man and quadrupeds, and in much larger quantity in the urine of birds, whether carnivorous or herbivorous, as in the pigeon and hawk tribes. In the urine of birds it forms the white part, in the form of urate of ammonia, and it is still found as such in guano—a substance produced by the long-continued action of the air on the urine (or excrement, for they are voided together) of sea-fowl. The only excrement of serpents, as, for example, of the boa constrictor, is a white semi-solid mass, which soon dries, and is pure acid urate of ammonia. In serpents, which are all carnivorous, it is very remarkable that the whole excreta (except occasionally hair and feathers, which pass undigested), should take the form of urate of ammonia. In diseased urine, uric acid is often deposited on cooling, and generally of a reddish color; it also constitutes the most frequent form of gravel and of calculus, when deposited within the bladder. Acid urate of soda is found in the chalk stones of gouty patients; and it is well known that gout is a disease closely allied to calculus of this kind.

It is best obtained from the excrement (or urine) of the boa, which is powdered, and dissolved in 40 parts of boiling water by the gradual addition of caustic potash, till the liquid is decidedly alkaline. The uric acid forms urate of potash, which dissolves, while the ammonia escapes. The hot liquid, being filtered to separate impurities (and with the above proportion of water it filters rapidly, while with less it crystallizes on the filter and chokes it up), is mixed with a decided excess of hydrochloric acid, when the uric acid is set free, and being insoluble, is deposited, at first, as a very bulky gelatinous hydrate, which in a few minutes spontaneously loses water, and shrinks into a crystalline heavy precipitate. This is well washed with cold water and dried in the air, when it forms a shining powder, composed of distinct but minute crystals. If made from a cold saturated solution of urate of potash, the crystals are much larger, but contain 17.5 per cent.; in this case 4 eq. of water are expelled at 212° , leaving the same substance as that precipitated from a hot solution, which, when dried in the air,

loses no weight at 212° . The latter is $C_{10}N_4H_2O_6 + H_2O = \overline{Ur} + H_2O$; the large crystals are a hydrate, $\overline{Ur}, H_2O + 4 \text{ aq.}$

If pure white fragments of the urine of the boa have been used, the above simple process yields uric acid chemically pure, even when the solution in potash has had a decided yellow color. This uric acid is snow-white, and is entirely dissipated by heat, leaving no trace of ashes. But if the boa's urine have been impure, or if calculi have been employed to yield uric acid, in both of which cases the alkaline solution is brown, often very dark, and yields a colored uric acid, or again, if we wish to extract uric acid from guano, we must first purify the urate of potash by evaporating the alkaline solution till it crystallizes in a mass, or passing carbonic acid through it to neutralize the free potash, when the acid urate of potash is deposited, and is washed on a filter with cold water, in which it is very sparingly soluble, till it is quite white. It is then dissolved in boiling water, and decomposed by hydrochloric acid as before. I have described thus minutely the preparation of pure and colorless uric acid, because none of the very interesting products derived from it can be obtained if we employ uric acid with even a very slight tinge of color. The presence of a mere trace of the coloring matter of urine I have found to exert a most remarkable influence on the oxidation of uric acid by nitric acid, an influence which I can only compare to that of a ferment in causing a peculiar decomposition to take place.

Uric acid requires 15,000 parts of cold and nearly 2,000 of hot water for solution, and its solution reddens litmus. It forms salts with bases, especially with the alcalies and alkaline earths, all of which are insoluble or sparingly soluble.

The salts of uric acid have been lately examined by Bensch, according to whom the common urates are acid salts, while the eq. of the acid is only half that above given, or $C_5N_2H_2O_3 = C_5N_2H_2O_3 + H_2O$. The neutral salts are $C_5N_2H_2O_3 + MO$, and the acid salts are $C_5N_2H_2O_3, MO + C_5N_2H_2O_3, H_2O$. Bensch has obtained the neutral salts of potash and soda, which are much more soluble than the well known urates of these bases, acid urates, according to Bensch. The neutral urate of potash dissolves in 35 parts of hot water, is alkaline, and is converted into the acid salt, both by water and carbonic acid. The acid salt requires 85 parts of boiling water for solution. The urates of soda are less soluble, and the acid urate of ammonia, the only salt formed with this base, dissolves in about 1,600 parts of water at 60° , and 240 parts at 212° .

The only other urates hitherto examined by Bensch are the acid salts of magnesia, lime, baryta, strontia, lead, and copper. It would appear that, adopting his formula, the uric acid has a most remarkable tendency to form acid salts, and as it appears also to form double salts, it is not easy to see why he halves the

formula of Liebig for the hydrated acid; since the above characters are those which distinguish bibasic acids, and it would appear more consistent with the newly observed relations of the acid, to express the formula of Liebig, $C_{10} N_4 H_4 O_4 = C_{10} N_4 H_2 O_4 + H_2 O$ by the following bibasic form, $C_{10} N_4 H_2 O_4 + 2 H_2 O$, than by the monobasic form, $2 (C_5 N_2 H O_2, H_2 O)$. If we adopt the bibasic formula, then the general formulæ for the neutral and acid salts as above given by Bensch, will become respectively, $C_{10} N_4 H_2 O_4 + 2 M O$, and $C_{10} N_4 H_2 O_4 + \begin{matrix} M O, \\ H O. \end{matrix}$

PRODUCTS OF THE OXIDATION OF URIC ACID.

Uric acid is very permanent under ordinary circumstances, but is readily oxidized by powerful oxidizing agents, such as peroxide of lead, peroxide of manganese, permanganate of potash, and nitric acid.

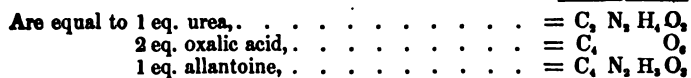
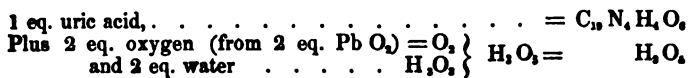
1. *Oxidation of Uric Acid by Peroxide of Lead.*—If uric acid be mixed with twenty parts of boiling water, and peroxide of lead added in small portions to the liquid kept boiling, the brown color of the oxide disappears, and a heavy white powder is formed. When we have added about two parts of the oxide for one of uric acid, or, at all events, when the oxide begins not to lose its brown color, the hot liquid is to be filtered, and on cooling it deposits a number of hard, brilliant white crystals, of which more are obtained on evaporation. The mother liquid at last crystallizes in a mass of very soluble prismatic crystals. These last are pure urea: the first crystals are allantoine, and the powder is oxalate of lead, mixed with a little carbonate, and with the excess of peroxide. Hence, the products of this oxidation are, urea, allantoine, and oxalic acid. After describing allantoine, we shall be able to explain the reaction.

Allantoine, $C_4 N_2 H_2 O_3$. SYN. *Allantoic Acid.*—This body was first observed in the allantoic fluid of the fetal calf, which is, in fact, the urine of the fetal animal. When this fluid is evaporated, it deposits crystals of allantoine, formerly called allantoic acid, which, however, is not an acid. Its occurrence in the allantoic fluid—that is, as an ingredient in urine—and its artificial production from uric acid by a process of oxidation, are facts of very great interest when viewed in connection. It is best obtained from uric acid, as above described. It is a very indifferent or neutral substance, and forms few compounds; only one, with oxide of silver, has been described, the formula of which is $C_4 N_2 H_2 O_3 + Ag O = 2$ eq. allantoine, minus 1 eq. water, and plus 1 eq. oxide of silver.

When boiled with alcalies, it is resolved into ammonia which escapes, and oxalic acid which combines with the alcali. In fact, both allantoine, $C_4 N_2 + H_2 O_3$, and oxalate of ammonia, $C_2 O_3$,

+ NH_3 , may be represented as formed of cyanogen and water, and it is obvious that the addition of 3 eq. of water to 1 eq. of allantoin gives $\text{C}_4\text{N}_4 + \text{H}_2\text{O}_6 = 2 (\text{C}_2\text{O}_2 + \text{NH}_3)$.

We can now explain the formation of allantoin.



Or, in the form of an equation,



That allantoin is closely related to uric acid and urea farther appears from the fact, that 1 eq. uric acid, 1 eq. urea, and 1 eq. water, added together, are exactly equal to the sum of 3 eq. allantoin: $C_{10} N_4 H_4 O_6 + C_2 N_2 H_4 O_2 + H O = C_{12} N_6 H_8 O_8 = 3 (C_4 N_2 H_2 O_2)$.

2. *Oxidation of Uric Acid by Peroxide of Manganese.*—This is performed much as the preceding, and there appear to be produced compounds, partly the same as those from peroxide of lead, partly different. Of the latter, one at least is crystallizable, but has not been sufficiently examined. The subject requires investigation.

3. *By Permanganate of Potash.*—In this oxidation also, some products appear, which are obtained by peroxide of lead, such as urea; and, in some forms of the experiment at all events, oxalic acid; but I have also observed the formation of a new acid, containing nitrogen, the precise nature and composition of which is not yet ascertained.

4. *By Nitric Acid.*—This mode of oxidation of uric acid has been minutely studied by Liebig and Wöhler, and they have shown that it yields a very large number of new and important products, among which is again found urea, and also, under certain circumstances, oxalic acid. The changes are best traced when colorless nitric acid of a considerable concentration, of Sp. G. 1.45, for example, is employed.

1. *Alloxan*.—When uric acid is added, in small portions, to this acid, it is dissolved with a gentle and uniform effervescence, due to the escape of pure carbonic acid and nitrogen gases, without any trace of the red vapors of nitrous acid. Heat is also developed, so that no external heat is required, and it may even be necessary to moderate the reaction by placing the vessel in cold water.

If too much uric acid be added at once, or if the mixture be allowed to get too hot, a violent reaction ensues, accompanied by copious red fumes, after which the experiment cannot succeed, and must be recommenced with fresh materials. The presence of a trace of the coloring matter of the urine infallibly causes this violent reaction, even with a much weaker nitric acid, and thus prevents us from obtaining the desired result, even to a small extent. In all these cases, the whole seems to be converted into oxalate and carbonate of ammonia. When the operation is properly managed, and a little practice makes it quite easy, there appear, in the warm liquid, after a certain quantity of uric acid has been dissolved, granular crystals of the new compound, alloxan. If more uric acid be added, it is still decomposed, and when the warm liquid (at about 120°) contains a great many crystals, it is allowed to cool, when the quantity of crystals greatly increases. They are now thrown on a filter stopped with asbestos, and when they have drained, the acid liquor still in their pores is displaced by a little ice-cold water, which is added till the droppings have only a slight acid taste. The crystals are now dissolved on the funnel with water at 120° , and the filtered solution evaporated at that or even a lower temperature, till, on being set aside, it deposits large transparent crystals of hydrated alloxan, which are chemically pure. The mother liquid of these crystals, being gently evaporated, yields more, and the final mother liquid, which is now rather acid, from nitric acid, is added to the original acid mother liquor, to be used for other purposes. By the above process, I have constantly obtained, without difficulty, upwards of from 90 to 105 parts of hydrated alloxan, quite pure, from 100 of uric acid, besides what remains in the mother liquid, and cannot be extracted in that form. Not more than 2 oz. or 3 oz. of nitric acid should be used in one operation, and this quantity will decompose about one-third of its weight of uric acid, or more.

The crystals of hydrated alloxan, when heated to 212° lose about 27 per cent. of water, = 6 eq. The dry or anhydrous alloxan, which may also be obtained in crystals when a saturated solution is evaporated in a warm place, is composed of $C_8 N_2 H_4 O_{10}$, which explains its formation from uric acid; for $C_{10} N_4 H_4 O_8 + O_2 + H_4 O_4 = C_8 N_2 H_4 O_{10} + C_2 N_2 H_4 O_2$; that is, uric acid, plus 2 eq. oxygen and 4 eq. water, yields 1 eq. alloxan and 1 eq. urea.

The urea, when formed, is in contact with hyponitrous acid (derived from nitric acid by the separation of 2 eq. oxygen), and is immediately decomposed by it, yielding oxide of ammonium, which combines with some free nitric acid, carbonic acid, and nitrogen, which two last escape as gases. $C_2 N_2 H_4 O_2 + N O_2 = N H_4 O + 2 C O_2 + N_2$. At the end of the operation, therefore, the acid liquid, which has deposited crystals of alloxan, contains nothing

but alloxan, nitrate of ammonia, and free nitric acid. We may therefore express the final result as follows: $C_{10} N_4 H_4 O_8 + 2 (H O, N O_2) + 2 H O = C_{10} N_4 H_4 O_{10} + (N H_4 O, N O_2) + 2 C O_2 + N_2$.

Alloxan is very soluble in water, also in alcohol. Its solution stains the skin pink, and gives to it a heavy sickly odor. Its taste is peculiar and almost acidulous; but, although it reddens litmus, it has not the chemical characters of an acid. It is a very remarkable substance, from the numerous transformations which it undergoes, when subjected to the action of different re-agents.

By the action of soluble fixed alkalies, it is converted into a powerful acid, alloxanic acid; by the action of ammonia it yields another acid, mykomelinic acid; boiled with peroxide of lead, it is converted into urea and carbonic acid; by boiling with nitric acid, it is changed into a new and powerful acid, parabanic acid; by the action of sulphuretted hydrogen and other deoxidizing agents, it yields a new compound, alloxantine; with hydrosulphide of ammonia it gives a new salt called dialurate of ammonia; with sulphurous acid it combines, forming a compound acid, alloxano-sulphurous acid; and with sulphite of ammonia it forms another new salt called thionurate of ammonia. Such are the compounds formed by the direct action of re-agents on alloxan; but many others are produced by the action of re-agents on these, singly or jointly. Thus, when alloxan and alloxantine are both present in a hot solution, ammonia causes the development of a deep purple color, and the deposition, on cooling, of the gold-green crystals of murexide; acids acting on thionurate of ammonia produce thionuric acid, uramile, and uramilic acid; acids acting on murexide, produce murexan; acids acting on a dialurate of ammonia separate dialuric acid; ammonia, acting on parabanic acid, converts it into a new acid, oxaluric acid; and by the action of heat on alloxanate of baryta, another new acid, mesoxalic acid, is produced. Alloxanic acid, when heated, yields leucoturic acid and difluan; and alloxantine when boiled with hydrochloric acid, yields alituric and dilituric acids. We shall endeavor briefly to trace the formation and the relations of these remarkable products.

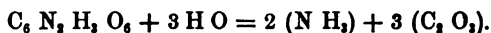
2. *Alloxanic Acid*.—Its formula $C_{10} N_4 H_4 O_8 + 2 H O$. It is therefore isomeric with alloxan, and differs from it in this, that 2 eq. water have become basic, and replaceable by metallic oxides. It is a bibasic acid. It is formed when solution of alloxan is mixed with barytic water, as long as the white precipitate first formed redissolves with a gentle heat. When it begins to be permanent, a drop or two of alloxan is added to clear all up; and on cooling, alloxanate of baryta is deposited in small white crystals. From this salt the acid is obtained by adding sulphuric acid, so as to separate all the baryta. The acid solution, on evaporating, yields crystals of alloxanic acid. The acid, when neutralized by

ammonia, forms, with nitrate of silver, a white precipitate, which, when boiled, becomes yellow, and is reduced with effervescence. When the solutions of its salts, with baryta, lime, and strontia, are boiled, they become turbid, depositing carbonates, while urea and a mesoxalate remain dissolved. The formula of the neutral alloxanates is $C_6 N_2 H_2 O_8, 2 M O + aq.$; that of the acid salts is $C_6 N_2 H_2 O_8, \frac{M O}{H O} \}$

Schlieper has lately studied the salts of alloxanic acid, and has confirmed the view above given. But he has also examined the products of decomposition of this acid, which are remarkable.

When a solution of alloxanic acid is boiled to dryness and pretty strongly heated in a capsule, carbonic acid is given off, and, when at last the residue ceases to yield any gas, and flows smoothly, the addition of water causes the separation of a crystalline powder in small quantity which is leucoturic acid; while the liquid contains a neutral body, difluan.

3. *Leucoturic Acid*.—Is white and crystalline, sparingly soluble, and not decomposed by nitric acid. It is dissolved by ammonia, with which it forms a crystallizable salt, and by potash, which, however, soon transforms it into oxalic acid and ammonia. Its composition is $C_6 N_2 H_2 O_8 = C_6 N_2 H_2 O_8 + H O$. It contains the elements of 2 eq. cyanogen, $C_4 N_2$, 1 eq. oxalic acid, $C_2 O_4$, and 3 eq. water, $H_2 O_3$. With 3 more eq. of water, it is resolved, when acted on by potash, into oxalic acid and ammonia.



4. *Difluan*.—The more soluble product of the decomposition of alloxanic acid, is precipitated from the aqueous solution by absolute alcohol as a flocculent mass, which in vacuo dries up to a light bulky white powder, which, when exposed to the air, very rapidly deliquesces: hence its name. It is an indifferent body, which is dissolved by potash, and rapidly decomposed in contact with that base. Its composition is, $C_6 N_2 H_4 O_8$, thus containing 1 eq. of hydrogen more, and 1 eq. of oxygen less, than leucoturic acid. When it is resolved into oxalic acid and ammonia, oxygen is probably absorbed from the air, unless hydrogen be given off, or some other new product formed. Thus, $C_6 N_2 H_4 O_8 + 2 H O + O_2 = 3 (C_2 O_4) + 2 (N H_3)$. This reaction has not been fully studied; but oxalic acid and ammonia are certainly produced.

Schlieper has observed a third product, along with leucoturic acid and difluan, which appears to contain 1 eq. of hydrogen more and 1 eq. of oxygen less than difluan. This, however, is not established, from the small amount of the substance obtained. The three formulæ exhibit the inverse variations in the hydrogen and oxygen.

Leucoturic acid	$C_8 N_2 H_2 O_6$
Diffuan	$C_8 N_2 H_2 O_6$
The third product	$C_8 N_2 H_2 O_6$

The formation of leucoturic acid and of diffuan from alloxanic acid is very simple.

1 eq. leucoturic acid,	$C_8 N_2 H_2 O_6$
1 eq. diffuan,	$C_8 N_2 H_2 O_6$
4 eq. carbonic acid,	$C_4 O_3$
1 eq. water,	$H O$
<hr/>	
2 eq. alloxanic acid,	$C_{12} N_4 H_4 O_{12}$

5. *Hydurilic Acid*.—In the preparation of alloxan, Schlieper, on one occasion, obtained a new body, which proved to be the ammonia salt of a new acid, hydurilic acid, $C_{12} N_4 H_4 O_{11}$. It is a bibasic acid, $= C_{12} N_4 H_2 O_9 + 2 H O$. It forms minute white prisms, sparingly soluble in cold water. It may be viewed as a compound of water and uryle ($C_4 N_2 O_4$), for $3 (C_4 N_2 O_4) + 10 H O = 2 (C_{12} N_4 H_4 O_{11})$. Hence its name.

It is evidently formed by an incomplete oxidation of uric acid, but Schlieper was not able to reproduce it.

With nitric acid, it yields a new acid, nitrohydurilic acid, of very similar external character, the empirical formula of which seems to be, $C_8 N_2 H_2 O_{14}$. This is equal to

1 eq. uryle,	$C_4 N_2 O_4$
1 eq. nitric acid,	$N O_3$
3 eq. oxygen,	O_3
2 eq. water,	$H_2 O$
<hr/>	
	$C_8 N_2 H_2 O_{14}$

And it is formed from

2 eq. hydurilic acid (anhydrous),	$C_{12} N_4 H_2 O_{10}$
3 eq. nitric acid,	$N_3 O_9$
9 eq. oxygen,	O_9
<hr/>	
3 eq. nitrohydurilic acid,	$C_{12} N_4 H_2 O_{12}$

Schlieper has further detected, in the same operation, in which he observed the hydurilic acid, another new acid, of which, however, little is known. Its empirical formula was found to be, $C_{12} N_4 H_2 O_8$. It has not been named.

6. *Mesoxalic Acid*.—Obtained, in combination with baryta, by boiling alloxanate of baryta; or combined with oxide of lead, by adding alloxan in solution, to a boiling solution of acetate of lead. The baryta salt is pale yellow, and sparingly soluble; the lead salt white and insoluble. The former is $C_2 O_4 \left\{ \begin{array}{l} Ba O \\ H O \end{array} \right.$, the latter $C_2 O_4, 2 Pb O$. The acid may be obtained from either of these salts; it crystallizes, is very sour, and is probably bibasic,

and has also, probably, the formula $C_6 O_4, 2 H O$. In that case, the anhydrous acid is very remarkable as a new compound of carbon and oxygen, of the same class as mellitic and oxalic acids: hence the name. It is characterized by forming, when neutralized by ammonia with nitrate of silver, a yellow precipitate, which, when heated, is reduced with brisk effervescence. This is evidently the cause of the reaction of alloxanic acid, above mentioned, with nitrate of silver. Mesoxalic acid deserves and requires a very careful investigation. Its formation from alloxan, or alloxanic acid, if its formula be $C_6 O_4$, is very easily explained: for 1 eq. alloxan, minus 1 eq. urea, gives 2 eq. mesoxalic acid: $C_6 N_2 H_4 O_{10} - C_2 N_2 H_4 O_2 = C_4 O_2 = 2 C_2 O_4$.

7. *Mykomelinic Acid*, $C_6 N_4 H_8 O_8$ —Is formed when ammonia acts on solution of alloxan; when a yellowish gelatinous precipitate of mykomelinate of ammonia soon appears. This boiled with dilute sulphuric acid yields a similar yellowish precipitate, which, when dry, forms a powder sparingly soluble in cold, more readily in hot water. It is decidedly acid. It is formed of the acid by the reaction of 2 eq. of ammonia on 1 eq. alloxan: $C_6 N_2 H_4 O_{10} + 2 N H_3 = C_6 N_4 H_8 O_8 + 5 H O$. It would appear to differ from allantoin, only by 1 eq. of water; for 2 eq. of allantoin are $C_6 N_4 H_8 O_8$.

8. *Parabanic Acid*, $C_6 N_2 O_4 + 2 H O$ —Is formed when alloxan or uric acid is heated with an excess of nitric acid, and the solution concentrated until, on cooling, it forms a soft crystalline mass. This is dried on a tile, and the dry crystals are purified by solution in hot water, filtration, and recrystallization. A large quantity of parabanic acid may easily be obtained from the acid mother liquors of alloxan. When pure, the acid is beautifully white and crystallized, very acid, and very soluble. It is characterized by its great permanence in the free state, for it may be boiled with nitric acid, as its preparation shows, and at the same time by its extreme proneness to change in contact with bases. Thus, if neutralized with ammonia in the warm solution, it deposits, on cooling, a crystallized salt, which is oxalurate of ammonia. The same change takes place with all bases except oxide of silver, so that the parabanate of silver is the only salt of this very powerful and remarkable acid which can be obtained. To be converted into oxaluric acid, parabanic acid only requires 3 eq. of water. The production of parabanic acid is very simple.
1. From uric acid: $C_4 N_2 H_4 O_6 + O_4 + H_2 O_2 = C_6 N_2 H_4 O_8 + 2 C O_2 + C_6 N_2 O_4, 2 H O$. 2. From alloxan: $C_6 N_2 H_4 O_{10} + O_2 = 2 C O_2 + 2 H O + C_6 N_2 O_4, 2 H O$.

9. *Oxaluric Acid*, $C_6 N_2 H_4 O_7 + H O$.—Formed by the action of bases on parabanic acid: $C_6 N_2 O_4 + K O + 3 H O = C_6 N_2 H_4 O_7, K O$. The acid is obtained by adding dilute sulphuric acid to a hot saturated solution of oxalurate of ammonia,

prepared by the action of ammonia on parabanic acid. On cooling, the oxaluric acid is deposited as a heavy white powder. When long boiled in water, it is decomposed into oxalate of urea and free oxalic acid. In fact, it contains the elements of 2 eq. oxalic acid and 1 eq. urea: $2 C_2 O_3 + C_2 N_2 H_4 O_2 = C_4 N_2 H_2 O_7, H O$. It is also characterized by forming with oxide of silver a white salt, which dissolves in hot water, and crystallizes beautifully on cooling.

The *oxalurate of ammonia*, $N H_4 O + C_2 N_2 H_2 O_7$ —Is formed whenever a solution of alloxan, or alloxantine in water, or of uric acid in nitric acid, is evaporated with excess of ammonia, and where coloring matter is present, as when ammonia is made to act on the acid in the mother liquors of alloxan, the oxalurate is often deposited in radiated hemispherical concretions, which sometimes attain the size of an inch or two in diameter, and are very hard. When decolorized by animal charcoal, it forms small, soft, flexible needles. I have found that this salt, when exposed to heat in a retort, yields ammonia, hydrocyanic acid, and much oxamide, besides water, and perhaps other products, while a dark residue is left.

10. *Thionuric Acid*, $C_2 N_2 H_2 S_2 O_4 = (C_2 N_2 H_2 O_2, 2 S O_2) + 2 H O$ —Is formed when sulphite of ammonia, with excess of base, is added to solution of alloxan, and the whole boiled for a few minutes, or until crystals appear in the hot liquid. On cooling it forms a semi-solid mass, from the separation of a large quantity of thionurate of ammonia in beautiful silvery crystals, which are to be washed with cold water, and dried on a tile. From this salt thionurate of lead is prepared, and this, being decomposed by sulphuric acid, yields thionuric acid. The acid is crystallizable, but very soluble. It is bibasic, and contains the elements of 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid, not however as such, for the elements of 2 eq. water have assumed the basic form.

Its most striking character is, that when its solution is heated it becomes turbid from the deposition of a new compound, uramile, and in the liquid sulphuric acid may now be found, which was not previously present: $C_2 N_2 H_2 O_2 + 2 S O_2 = C_2 N_2 H_2 O_2 + 2 S O_2$; so that the sulphurous acid obtains oxygen from the rest of the acid, and becomes sulphuric acid, leaving uramile, $C_2 N_2 H_2 O_2$.

Thionurate of Ammonia, $(C_2 N_2 H_2 O_2, 2 S O_2) + 2 N H_4 O + 2 aq$.—Is formed as above described. When its solution is mixed with 1 eq. of hydrochloric acid, half the ammonia is removed, and by evaporation we obtain acid thionurate of ammonia in minute silky needles. But when the hot solution of thionurate of ammonia is mixed with an excess of acid, the thionuric acid is set free and instantly decomposed, uramile being deposited. Little is known of the other thionurates.

11. *Uramile*, $C_8 N_2 H_8 O_8$.—Its formation has been described above. It occurs either as a crystalline powder, or in dendritic or feathery crystallizations, of very beautiful aspect. It dissolves in ammonia and potash, and the solution absorbs oxygen; becoming purple, and depositing green crystals of murexide, or of potassium-murexide. When boiled with peroxide of mercury, and a very little ammonia, it is also converted into murexide. Boiled with caustic potash, or with dilute acids, it is said to yield uramilic acid. Nitric acid reconverts it into alloxan.

12. *Uramilic Acid*.—Obtained, by Liebig and Wöhler, by evaporating acid thionurate of ammonia, or uramile, with dilute sulphuric acid; also, it is said, by boiling uramile with potash. It appeared to these chemists as fine prisms, very soluble in water, and its analysis indicated the formula $C_{16} N_4 H_{10} O_{16}$; which might be derived from 2 eq. uramile by the loss of 1 eq. ammonia, and the addition of 3 eq. water: $2 (C_8 N_2 H_8 O_8) + 2 H O - N H_3 = C_{16} N_4 H_{10} O_{16}$. But this acid has not been again obtained, and its existence is still doubtful.

13. *Alloxantine*, $C_8 N_2 H_8 O_{10}$.—Obtained in large quantity by diluting the acid mother liquid of alloxan with 3 or 4 parts of water, and passing a current of sulphuretted hydrogen through it. In a short time sulphur is deposited, and then white crystals of alloxantine. When a large quantity has formed, it is collected with the sulphur, on a filter, washed with a little cold water, and the filter with its contents then boiled with a large quantity of water. The solution, filtered while hot, and with the addition of a few drops of hydrochloric acid, deposits, on cooling, a large crop of pure crystals of alloxantine. The acid liquid, filtered from the first deposit, often, on standing a day or two, deposits a large additional quantity of alloxantine. This always happens, if too much sulphuretted hydrogen has been used; for that converts the alloxantine partially into dialuric acid, which is more soluble, but by absorbing oxygen from the air, is reconverted into alloxantine, and thus deposited.

Alloxantine may also be obtained by deoxidizing a pure solution of alloxan, either by sulphuretted hydrogen, or by other deoxidizing agents; or by heating a solution of alloxan to the boiling point, either by itself or with the addition of dilute mineral acids, when alloxantine is formed and deposited on cooling. But the process above given for converting into alloxantine the alloxan of the acid mother liquor, which cannot be purified by crystallization, is so productive, and yields alloxantine so pure, that, if we have to prepare alloxan, we need never be at a loss for alloxantine.

The formation of alloxantine from alloxan by sulphuretted hydrogen is easily explained, for these compounds only differ by 1 eq. hydrogen, which the alloxan takes from sulphuretted hydrogen. Oxidizing agents, by converting this hydrogen into water,

readily reconvert alloxantine into alloxan: $C_8 N_2 H_2 O_{10} + O = H O + C_8 N_2 H_4 O_{10}$.

Alloxantine forms white, hard, brilliant crystals, which never exceed a certain small size. It is very sparingly soluble in cold water, much more so in hot water. Its solution is characterized by giving with solution of baryta a deep violet precipitate, which with excess of baryta, changes to white; and by instantly reducing nitrate of silver, forming a black powder of silver, the alloxantine passing into alloxan, or oxaluric acid. The crystals of alloxantine, heated to 300° , lose 3 eq. of water.

In the preparation of alloxan, it is necessary, as has been stated, to be very careful that the first solution of the crystals formed in the nitric acid should not be heated too strongly, because, as this solution contains free nitric acid, alloxantine is formed at a certain temperature; and besides, even a pure solution of alloxan, if boiled, is partly converted into alloxantine. The action of diluted nitric and other mineral acids on alloxan is to produce, from 2 eq. alloxan, 1 eq. alloxantine, 3 eq. oxalic acid, 1 eq. ammonia, and 1 eq. cyanic acid, the latter, with 3 eq. water, producing bicarbonate of ammonia. When solution of alloxan is boiled alone, it is converted into alloxantine, parabanic acid, and carbonic acid: $3 (C_8 N_2 H_4 O_{10}) = 2 (C_8 N_2 H_2 O_{10}) + C_8 N_2 H_2 O_6 + 2 C O_2$.

In all these, or in similar cases, the presence and the relative proportion of alloxantine contained in alloxan at any period, may be judged of by the color of the precipitate formed in baryta. If pure white, no alloxantine is present; if slightly pink, it is present in small quantity; if deep violet, all, or nearly all, the alloxan has been converted into alloxantine.

It is when both alloxan and alloxantine are present, that the addition of ammonia produces the deep purple color, and the green crystals of murexide. When ammonia acts on alloxantine alone, it gives rise to uramile, and, finally, to oxalurate of ammonia.

One most remarkable change which alloxantine undergoes is that caused by the further action of sulphuretted hydrogen. If that gas be passed through a hot solution of alloxantine, sulphur is precipitated, and an acid liquid is obtained, which, if neutralized by carbonate of ammonia, forms a salt in soft white silky crystals, the dialurate of ammonia. Alloxantine, by the action of hydrogen, which removes 1 eq. oxygen, is converted into dialuric acid.

14. *Dialuric Acid*, $C_8 N_2 H_2 O_7 + H O = C_8 N_2 H_4 O_8$.—Produced by the action of sulphuretted hydrogen on alloxantine: $C_8 N_2 H_2 O_{10} + H S = S + 2 H O + C_8 N_2 H_4 O_8$. It is best obtained, in combination with ammonia, by adding a slight excess of hydrosulphide of ammonia to a solution of alloxan or alloxantine, when a copious crystalline precipitate appears. This, when boiled, dissolves in the liquid, and on cooling is deposited in minute silky prisms, which are white, but in drying become pink or

even deep red. They should be washed on the filter, first with diluted hydrosulphide of ammonia, then with alcohol, to which a little hydrosulphide has been added; and lastly, with pure alcohol; and dried by pressure in blotting-paper, and in the vacuum of the air-pump. They may thus be obtained white, or very nearly so; and when once quite dry, they are permanent. When this salt is dissolved in hot and moderately strong hydrochloric acid, crystals of dialuric acid are deposited on cooling. These crystals resemble somewhat those of alloxantine, but are larger, and not so brilliant. Their solution, and the crystals themselves under water, absorb oxygen, and are soon changed into alloxantine, from which dialuric acid only differs by 1 eq. oxygen and 1 eq. water.

Dialuric acid is a powerful acid. Its salts are insoluble or sparingly soluble, and only permanent in the dry state. The dialurate of ammonia, above described, is the most interesting.

15. *Alituristic Acid*. — This acid is formed when alloxantine is boiled with hydrochloric acid, and was discovered by Schlieper. It is soluble in 15 or 20 parts of hot water, and is deposited on cooling as a bulky crystalline powder. It is not altered by nitric acid. Its formula is $C_8N_2H_2O_4 = C_8N_2H_2O_3 + H_2O$. When heated with potash, ammonia is disengaged, and the addition of an acid causes a precipitate of a new body, apparently composed of $C_{10}N_2H_2O_{10} + K_2O$. Such a body might be formed from 3 eq. alituristic acid + 4 eq. oxygen + 2 eq. water, the whole — 1 eq. ammonia.

16. *Dilituristic Acid*. — This is found in the liquid obtained when the preceding acid is purified from alloxantine by nitric acid, in combination with ammonia. The acid retains the ammonia with such force that it has not yet been obtained in a separate form. The ammoniacal salt is $C_8N_2H_2O_3 + NH_4O + H_2O$; and the acid is supposed to be bibasic, $C_8N_2H_2O_3 + 2H_2O$.

It is probably a coupled acid, for it contains the elements of 3 eq. cyanic acid, 2 eq. carbonic acid, and 3 eq. water: $3(C_2N_2O) + 2CO_2 + 3H_2O = C_8N_2H_2O_{10}$. The silver salt explodes when heated, which is rather favorable to this view.

17. *Murexide*. *SYN. Purpurate of Ammonia*. — Formed, as already mentioned, when ammonia acts on a solution containing both alloxan and alloxantine, which explains its production when ammonia is added to the solution of uric acid in dilute nitric acid, after evaporation to a certain extent; also, when uramile or murexan is boiled, with red oxide of mercury or oxide of silver, in water, with a few drops of ammonia, or when uramile or murexan is dissolved in ammonia and exposed to the atmosphere; and in a great variety of circumstances from all the preceding compounds, or nearly all of them.

On the small scale, 4 grains of alloxantine and 7 grains of hydrated alloxan, are dissolved together in $\frac{1}{4}$ oz. by measure of water by boiling, and the hot solution added to $\frac{1}{4}$ oz. by measure

of a saturated or nearly saturated solution of carbonate of ammonia, the latter being cold. This mixture has exactly the proper temperature for the formation of murexide; and it does not, owing to its small bulk, remain too long hot. It instantly becomes intensely purple, while carbonic acid is expelled; and as soon as it begins to cool, the beautiful green and metallic-looking crystals of murexide appear. As soon as the liquid is cold, these may be collected, washed with a little cold water, and dried on a filtering paper. I have obtained them by the above process, and on this small scale, of from 2 to 3 lines in length. When made with larger quantities, the crystals are always smaller, owing, probably, to some effect of the slower cooling of the larger mass of liquid, as continued heat is not favorable to their formation. If we do not care about having the finest crystals, we may prepare murexide in large quantity by adding solution of alloxan to a boiling solution of alloxantine, and cautiously adding cold solution of carbonate of ammonia, till the mixture has become nearly black, and the green crystals begin to appear. The vessel being removed from the fire, deposits a very large quantity of murexide. In these processes, the residual liquid is still colored, and is alkaline from excess of ammonia; if kept, it loses the red color, becomes yellowish, and is evaporated, yields much alloxanate of ammonia in crystals.

Murexide is one of the most beautiful products of chemistry: the crystals are metallic green by reflected light, like the cantharides fly or the gold beetle, and deep red by transmitted light. Their solution is deep purplish red, and they dissolve in potash with the most splendid purplish blue color that can be imagined; this, however, soon disappears. When their solution is acted on by a dilute mineral acid, it is decolorized, and deposits a shining scaly crystalline powder, of a pale yellow color, which is murexan. The same compound is obtained when acids are added to the solution of murexide in potash, after the purple tint has disappeared on digestion in a gentle heat.

The composition of murexide is uncertain, and there are different views of its constitution. According to some it is a salt of ammonia; and this view is supported by the fact that, with salts of baryta and oxides of lead and silver, it yields purple salts, which, according to Fritzsche, contain the same acid that in murexide is combined with ammonia, and which may be called purpuric acid. But murexide is not a compound of ammonia with the purpuric acid of Prout; for when that body (murexan) is dissolved in ammonia, it only forms murexide by absorbing oxygen from the air, and yields other compounds at the same time. Again, the action of sulphuretted hydrogen is inconsistent with the view of murexide being a salt of ammonia, and in many of its relations it more resembles a neutral body — such as a compound of amide.

Its products of decomposition are very numerous, and altogether the subject is one of much difficulty. Possibly there may be two substances similar in appearance, but distinct in constitution; one a salt of ammonia, the other an indifferent body, or an amidide. The great discrepancy in the results of analysis, as obtained by Liebig and Wöhler on the one hand, and Fritzsche on the other, as well as some differences in the properties ascribed to it by different chemists, lead to some such conclusion. The formula considered by Liebig and Wöhler the most probable, all things considered, but not established, is $C_{12} N_2 H_6 O_8$; another somewhat less probable, is $C_{20} N_4 H_{10} O_{14}$. Both of these will enable us to account for its production, in different circumstances. The formula of Fritzsche, which agrees with his analysis, is $C_{16} N_4 H_8 O_{11} = N H_3 + C_{16} N_4 H_8 O_{11}$. The salt formed with nitrate of silver is, $C_{16} N_4 H_8 O_{11} + Ag O$, which would exhibit the unusual phenomenon of ammonia, instead of oxide of ammonium, being replaced by oxide of silver; and the baryta compound is $C_{16} N_4 H_8 O_{11} + H O + Ba O$. Admitting the formulæ of Fritzsche for the silver and barium compounds to be correct, these are not demonstrated to be salts of purpuric acid; but besides this, his formula for murexide does not enable us to explain its production in any case. In these circumstances, we shall not attempt to explain the formation of murexide, farther than to point out that it appears to require the presence of a compound intermediate between alloxan and alloxantine (the former losing oxygen, the latter gaining it), and of ammonia; and that it is not the only product.

18. *Murexan*. SYN. *Purpuric Acid*, $C_6 N_4 H_4 O_8$?—Formed by the action of acids on murexide, but along with several other products. It appears as a shining powder, composed of scales, generally pale yellow, sometimes pale brown, never quite white. It is insoluble in water or nearly so, but the liquid filtered from it has always a peculiar opalescent aspect and play of colors. It dissolves in potash and ammonia, and the solutions become purple, by absorbing rapidly oxygen from the air, and finally deposit green crystals. When boiled with peroxide of mercury, water, and a little ammonia, it yields murexide. It dissolves in oil of vitriol, and is precipitated unchanged by water. In all these characters, except in its external aspect, it coincides entirely with uramile, and it is not impossible that it may be hereafter found to be uramile, disguised by the presence of a foreign substance. For the present, however, its analysis compels us to distinguish it from uramile.

Having now described the numerous products of the oxidation of uric acid by nitric acid, we are prepared to understand the nature of the radical supposed to be common to most of these compounds.

Uryle. $U1 = C_4 N O_4 = 4 C O + 2 C_2 N$.

SYN. Cyanoxalic Acid.—This radical is unknown in the separate form. It contains the elements of four eq. carbonic oxide or 2 eq. oxalyle ($C_2 O_2$), and 2 eq. cyanogen. Hence the name cyanoxalic acid. Assuming it to exist, we have the following series :

Rational formulæ.	Names.	Empirical formulæ.
$U1 + 1 \text{ eq. urea}$	= Uric acid,	= $C_8 N_4 H_4 O_4$
$U1 + O + 5 H O$	= Alloxantine,	= $C_8 N_4 H_4 O_6$
$U1 + O_2 + 4 H O$	= Alloxan,	= $C_8 N_4 H_4 O_5$
$U1 + 4 H O$	= Dialuric acid,	= $C_8 N_4 H_4 O_4$
$U1 + 10 H O$	= Hydurilic acid,	= $2(C_4 N_2 H_2 O_{10})$
$U1 + N O_2 + O_2$	} = Nitrohydurilic acid,	= $C_8 N_4 H_4 O_{14}$
$+ 2 H O$		
$U1 + N H_3 + 2 H O$	= Uramile,	= $C_8 N_4 H_4 O_4$
$U1 + O_2 + 4 H O$	} = Thionuric acid,	= $C_8 N_4 H_4 O_{14} S_2$
$+ N H_3 + 2 S O_2$		

The ready conversion of these compounds one into another is a strong argument for the existence of the radical uryle. But the rational formulæ above given do not represent what we suppose to be the actual arrangement; they only point out by what simple means, as the addition or removal of oxygen, or ammonia, or water, the elements of the new compounds might be supplied. The other derivatives of uric acid are probably compounds of different radicals: thus, parabanic and oxaluric acids each contain only 6 eq. of carbon, and cannot, therefore, be compounds of uryle.

The above brief sketch of the products derived from uric acid, will serve to show the inexhaustible variety of new products, which one complex body may yield. Notwithstanding all that has been done, we must consider this subject as merely opened up and a farther prosecution of it will infallibly lead to many interesting and valuable results.

APPENDIX TO URIC ACID.

1. *Uric or Xanthic Oxide.*—This is a very rare ingredient of urinary calculi. Its formula is $C_8 N_4 H_4 O_6$, which taken double differs from uric acid only by 2 eq. oxygen. Hence its name of uric oxide. It is soluble in potash and precipitated by acids as a white powder. It dissolves in nitric acid, and the solution evaporated to dryness, leaves a yellow residue: hence the name of xanthic oxide. It is said to occur in small quantities in some kinds of guano.

2. *Cystic Oxide*, $C_8 N_4 H_4 O_4 S_2$.—Another very rare form of calculus. It dissolves both in acids and alcalies, and has the characters of an organic base, forming crystalline compounds with acids. It is remarkable from the large quantity of sulphur it contains.

3. *Guanine*, $C_{10} N_4 H_4 O_6$.—This compound has been discovered quite recently in guano, by Unger, who at first supposed it to

be identical with uric or xanthic oxide, but subsequently found it to be a distinct compound. It seems to be a base somewhat analogous to urea; for it unites with hydrochloric, sulphuric, and nitric acids, forming crystallizable salts, among which are acid salts, with hydrochloric and nitric acids, a very rare phenomenon.

Guanine is a white powder, insoluble in water. Like other organic bases, it forms a double salt when its hydrochlorate is mixed with bichloride of platinum. This salt crystallizes in fine orange yellow crystals, the formula of which is $(C_{10} N_4 H_5 O_6, H Cl) + 2 Pt Cl_2 + 4 H O$. It is remarkable that guanine forms no basic salts, as most weak bases do, but only neutral and acid salts.

Hyperuric Acid (?).—This acid was also discovered by Unger, who obtained it by acting on guanine with a mixture of hydrochloric acid and chlorate of potash. Its formula, according to Unger's experiments, is $C_{10} N_4 H_5 O_9$, which differs from uric acid by 1 eq. water, and 2 eq. oxygen; hence the name. Unger conjectures it, from the analysis of the silver salt, to be bibasic, $C_{10} N_4 H_5 O_9 + 2 H O$; but the want of material has prevented him from fully investigating this curious acid; and he marks its formula, and even its name as doubtful.

The acid forms short rhombic prisms, colorless, and of brilliant lustre. When heated, it yields hydrated cyanic acid, water and a residue of carbon. This might occur with the formula above given, for $C_{10} N_4 H_5 O_9 = 4 (C_2 N O, H O) + H O + C_2$.

XIII. BENZOYLE. $Bz = C_{11} H_7 O_2$.

This is the radical of benzoic acid, of oil of bitter almonds, and of an extensive series of compounds. The radical is not yet known with certainty in the separate form, although a compound exists, having the same composition. (See *Benzile*.) We shall describe first the benzoic acid, and afterward the other compounds derived from, or connected with it.

1. BENZOIC ACID. $C_{11} H_7 O_2, H O = Bz O, H O$, or $Bz O_2, H$.

This acid is found in gum benzoin, mixed with some resins; and it also occurs in the urine of herbivorous animals, under certain circumstances. It is also formed by the oxidation of the oil of bitter almonds. It may be obtained from benzoin by sublimation, the powdered gum being gently heated on an iron plate forming the bottom of a broad and short cylinder, the top of which is covered with bibulous paper pasted tightly down to the sides, while another cylinder slides over the upper end of the first, to prevent the escape of the acid. The vapors of the acid, which is very volatile, pass through the paper, and forming crystals, are there retained, falling on its upper surface. The following method, however, is far more productive, as in the process of sublimation some of the acid is always decomposed. Benzoin is dissolved in strong

alcohol, and to the hot solution there is added hydrochloric acid in quantity sufficient to precipitate the resin; the whole is then distilled. The benzoic acid passes over under the form of benzoic ether (benzoate of oxide of ethyle); and when the greater part of the liquid has been distilled off, water is added to the residue, and distilled as long as any ether passes over with it. When this ceases, the hot water remaining in the retort is filtered, and on cooling deposits part of the benzoic acid in crystals. The benzoic ether and all the distilled liquors are now treated with caustic potash, until all the ether is decomposed, and the solution, now containing benzoate of potash, is heated to boiling, and supersaturated with hydrochloric acid. On cooling, it deposits the benzoic acid in crystals. By this means the whole benzoic acid of the benzoin is obtained.

Benzoic acid forms fine light prismatic crystals, or flexible pearly scales. When pure, it has no smell, but by heat it acquires the odor of benzoin or of vanilla, and as commonly prepared it has a very pleasant odor, derived from the presence of some foreign compound which accompanies the acid, and is not easily separated from it. It is very fusible and volatile, and its vapors are very irritating, provoking cough. It is inflammable, burning with smoke. It is sparingly soluble in cold water, more so in boiling water; it dissolves also in alcohol and ether.

With bases it forms salts, many of which are crystallizable. Their general formula is $Bz O, M O$, or $Bz O_2, M$. When the alkaline and earthy benzoates are heated in close vessels, they yield carbonates, while new products distil over, such as benzene, benzole, naphthaline, &c. The benzoate of peroxide of iron, $3 Bz O + Fe_2 O_3$, has a reddish white color, and is insoluble. Benzoic acid, in the form of benzoate of ammonia, is therefore sometimes used as a means of separating peroxide of iron from some other bases.

But its use requires many precautions, and it is quite inapplicable if alumina, glucina, yttria, or zirconia be present. Benzoate of silver, $Bz O, Ag O$, is sparingly soluble, and when formed in hot solutions crystallizes on cooling.

2. HYDURET OF BENZOYLE. $C_{14} H_6 O_2 = Bz H$.

SYN. Essential Oil of Bitter Almonds.—When bitter almonds, after being macerated with water for a day or two, are distilled with the water, there is obtained a fragrant oily liquid, heavier than water, which contains, besides hyduret of benzoyle, benzoic acid, hydrocyanic acid, and benzoine, a solid compound isomeric with the hyduret of benzoyle. To purify it, this oily liquid is distilled along with a mixture of protochloride of iron and slacked lime, which retain the two acids, and the benzoine remaining behind, the pure hyduret passes over.

It is a colorless transparent liquid, of a high refractive power. It has a peculiar and very powerful smell, and it is on this account that the crude oil is so much used in perfumery. Its odor has been compared to that of hydrocyanic acid, but this has arisen from the fact that the crude oil contains both: for on comparing the two, no similarity can be perceived. It ought, however, to be borne in mind that the commercial oil is highly poisonous, not only because it contains hydrocyanic acid, but because the hyduret of benzoyle is poisonous. Hyduret of benzoyle boils at 356° .

When exposed to the air, it absorbs 2 eq. of oxygen, and is converted into pure crystallized benzoic acid: $\text{Bz H} + \text{O}_2 = \text{Bz O}, \text{H O}$. Heated with caustic potash in close vessels, it yields benzoate of potash and hydrogen gas, which is disengaged: $\text{K O}, \text{H O} + \text{Bz H} = \text{K O}, \text{Bz O} + \text{H}$. It is still more easily converted into benzoate of potash by an alcoholic solution of potash: the alcohol here swims above the salt, and holds in solution an oily matter not yet examined.

When hyduret of benzoyle is mixed with a little hydrocyanic acid, and placed in contact with aqua potassæ, lime-water, or baryta water, it is gradually converted into the solid crystalline compound, isomeric with itself, which is called benzoine. When mixed with aqua ammoniæ, and gently heated, it produces a new compound, hydrobenzamide. With chlorine and bromine, if dry, it yields chloride and bromide of benzoyle, with hydrochloric and hydrobromic acids; if water be present, benzoic acid is likewise formed, part of which combines with some unchanged hyduret of benzoyle.

3. *Chloride of Benzoyle*, formed by the action of dry chlorine on the hyduret, is a colorless liquid, of a strong disagreeable odor. It is formed as follows: $\text{Bz H} = \text{Cl}_2 = \text{Bz Cl} + \text{H Cl}$. With the alkalies it yields benzoate of the alkali, and chloride of the metal: $\text{Bz Cl} + 2 \text{K O} = \text{K O}, \text{Bz O} + \text{K Cl}$. With dry ammonia it yields benzamide; with alcohol it produces benzoic ether and hydrochloric acid: $\text{Ae O}, \text{H O} + \text{Bz Cl} = \text{Ae O}, \text{Bz O} + \text{H Cl}$. When acted on by metallic bromides, iodides, sulphides, or cyanides, it produces metallic chlorides, and bromide, iodide, sulphide or cyanide of benzoyle. The bromide of benzoyle is a crystalline solid, in other respects analogous to the chloride. The iodide and sulphide of benzoyle are also crystallizable: the cyanide is a liquid having an odor like that of cinnamon.

4. **BENZAMIDE.** $\text{C}_{14} \text{N H}, \text{O}_2 = \text{C}_{14} \text{H}_5 \text{O}_2 + \text{N H}_2 = \text{Bz Ad}$.

This compound is formed when dry ammonia acts on chloride of benzoyle, $\text{Bz Cl} + \text{N H}_2, \text{H} = \text{Bz}, \text{N H}_2 + \text{H Cl}$: also when hippuric acid (which see) is boiled with peroxide of lead. When prepared from the chloride, it is accompanied by sal ammoniac, formed by the hydrochloric acid produced, with the excess of

ammonia. This is removed by cold water; and the benzamide, being dissolved in hot water, crystallizes on cooling. It forms fine soft needles or pearly scales, very fusible and volatile. Like other amidides, it yields ammonia when boiled with alcalies, while a benzoate is formed.



This compound is obtained by adding to distilled water some crude oil of bitter almonds, which always contains hydrocyanic acid (see *Amygdaline*), and evaporating to dryness along with some hydrochloric acid. From the dry mass, ether dissolves the new acid, which it deposits as a crystalline powder by evaporation. In this process, the hydrocyanic acid, under the influence of hydrochloric acid, is converted, along with the elements of water, into formic acid and ammonia. The latter combines with the hydrocyanic acid, the former with the hyduret of benzoyle, yielding formobenzoilic acid. With bases this acid forms salts, in which the quantity of base neutralized is exactly that which would be neutralized by the formic acid alone. Their formula is $M O + Fo O_2, Bz H$; by which it is seen that the hyduret of benzoyle has entered into the radical of the acid, without altering its power of saturation; and perhaps the rational formula of the acid ought rather to be, $(Fo O_2, Bz H) + H$; and that of the salts, $(Fo O_2, Bz H) + M$; which exhibits this view still more clearly.



This compound is formed when moist chlorine is passed through the oil of bitter almonds. Hydrated benzoic acid is formed, which unites with the unchanged hyduret. The action of moist chlorine in producing hydrated benzoic acid is as follows: $Bz H + 2 H O + Cl_2 = 2 H Cl + Bz O, H O$. The new compound is crystalline, insoluble in water, soluble in alcohol and ether. It is volatile without decomposition. An alcoholic solution of potash dissolves it, and converts it into benzoate of potash.



This acid is found in very considerable quantity in the urine of herbivorous animals, such as the horse and cow, more especially when stall-fed. It has also been lately discovered by Liebig in human urine. It is easily obtained by evaporating gently to a small bulk the fresh urine of the horse or cow, and acidulating with hydrochloric acid. On standing, the liquid deposits brown crystals of hippuric acid, which may be decolorized by a little bleaching liquor and hydrochloric acid.

The pure acid forms pretty large semi-opaque, four-sided prisms sparingly soluble in cold water, very soluble in hot water,

and in alcohol. When heated, it melts, and gives off benzoic acid, benzoate of ammonia, and an oily matter, which has a very fragrant odor like that of the tonka bean. By nitric acid it is converted into benzoic acid.* Heated with peroxide of manganese and sulphuric acid, it yields ammonia, carbonic acid, and benzoic acid; boiled with peroxide of lead, it yields benzamide and carbonic acid.

With bases it forms salts, most of which are soluble and crystallizable.

Hippuric acid may be viewed in two ways; first, as a compound of benzamide with an acid, $C_4H_2O_2$ (fumaric or aconitic acid?) and it is remarkable that Schwarz, who has lately studied the hippurates, observed a very great similarity to the fumarates; as if the hyduret of benzoyle were simply taken up into the molecule of these salts, without much affecting their properties; secondly, as composed of hyduret of benzoyle, hydrocyanic acid, and formic acid. Either view readily accounts for its easy decomposition into benzoic acid and other products. As an ingredient of the urine, this acid is important; and we shall hereafter see that benzoic acid, taken into the system, appears in the urine as hippuric acid.

Dessaigues has recently shown, that, when hippuric acid is boiled with stronger acids for some time, it is decomposed, and yields benzoic acid, which crystallizes on cooling; while the mother liquid, on farther evaporation, yields fine crystals of the salts formed by the combination of sugar of gelatine (see *Gelatine*), with the acid employed. In fact, sugar of gelatine, according to Dessaigues, is a basis quite analogous to urea; and its salts, with the mineral acids, form double salts, and appear to act as acids, which is also the case with urea. If to

Hippuric acid,	$C_{10}N_2H_8O_6$
We add 2 eq. water,	H_2O_2

	$C_{10}N_2H_{10}O_6$
And from the sum deduct 1 eq. hydrated benzoic acid,	$C_{14}H_8O_6$

There remains, $C_6N_2H_8O_4$

And this is the formula which Gerhardt has recently proposed for sugar of gelatine. Whether this formula, however, or those of Mulder and Boussingault, be preferable, it is certain that the salts, obtained as above, by Dessaigues, with nitric, hydrochloric,

* M. BERTAGNINI has lately ascertained, that if nitro-benzoic acid be taken into the stomach, it passes into the urine in the form of a new acid, the nitro-hippuric $C_{10}N_2H_8O_{10}$. This acid may also be obtained by acting on hippuric acid with a mixture of fuming nitric and sulphuric acids. When it is heated with hydrochloric acid, it is resolved into Glycocoll and nitro-benzoic acids. B.

and sulphuric acids, are not distinguishable from those made with sugar of gelatine prepared from gelatine. Moreover, the sugar itself, separated from these salts, was found identical in properties with that from gelatine. The analysis of the sugar produced by the new method, which seems to be very pure, will no doubt settle the question as to the true formula of sugar of gelatine.

PRODUCTS OF THE DECOMPOSITION OF THE COMPOUNDS OF BENZOYLE.

1. HYPOSULPHOBENZOIC ACID. $C_{14}H_4O_3 + S_2O_2 + 2H + O$.

A bibasic acid. Formed when anhydrous sulphuric acid acts on crystallized benzoic acid, $C_{14}H_4O_3$, $H O + 2 S O_2 = C_{14}H_4O_3 + S_2O_2 + 2 H O$. The acid is soluble and crystallizable, and forms with baryta a soluble and crystallizable salt from which the acid may be obtained by the action of sulphuric acid. It forms two series of salts, one with 2 eq. of fixed base, the other with 1 eq. of fixed base and 1 eq. of water.

2. BROMOBENZOIC ACID. $C_{14}H_4BrO_3 + 2 H O$.

A bibasic acid. When the vapor of bromine is allowed to act on benzoate of silver at the ordinary temperature, there is produced this acid, along with bromide of silver and hydrobromic acid. 2 eq. of benzoate of silver and 4 eq. of bromine yield 1 eq. bromobenzoic acid, 1 eq. hydrobromic acid, and 2 eq. bromide of silver. $2(C_{14}H_4O_3 Ag O) + Br_2 = C_{14}H_4BrO_3 + H Br + 2 Ag Br$. Ether dissolves the acid and deposits it on evaporation, in a confused mass of crystals, very sparingly soluble in water. When the acid crystallizes, it takes up 2 eq. of water. With bases it forms salts, which are generally soluble and crystallizable. Their general formula is $C_{14}H_4BrO_3, 2 M O$.

3. BENZOLE. $C_{12}H_6$.

SYN. *Benzine*. *Benzène*. *Phène*.—Occurs in the volatile liquids condensed from oil gas; but is best obtained in a state of purity by distilling 1 part of crystallized benzoic acid with 3 of slaked lime. It is a limpid, colorless liquid, of an agreeable ethereal odor. Its Sp. G. is 0.85; it boils at 186° , and at 32° it becomes solid. It is insoluble in water, soluble in alcohol and ether. In its formation, 1 eq. of benzoic acid yields 2 eq. carbonic acid and 1 eq. benzole, the carbonic acid uniting with the lime, $C_{14}H_4O_3, H O = C_{12}H_6 + 2 C O_2$.

4. *Sulphobenzide*, $C_{12}H_6S O_2$.—When anhydrous sulphuric acid acts on benzole, a viscid mass is formed, from which, by the addition of water, is separated a new compound, which may be dissolved and crystallized by means of ether. $C_{12}H_6 + S O_2 = H O + C_{12}H_6, S O_2$. Sulphobenzide is quite neutral.

5. *Hyposulphobenzidic Acid*.—This acid is found in the liquid from which the preceding compound has been deposited. Its formula is $C_{12}H_4S_2O_4 + O$. It may be viewed as formed by the action of 2 eq. of dry sulphuric acid on 1 eq. of benzole, $C_{12}H_4 + 2 S O_2 = C_{12}H_4S_2O_4 + H O$; or as formed by the combination of sulphobenzide with oil of vitriol, $C_{12}H_4S_2O_4 + H O, S O_2$. Either view readily explains its formation. The acid is best obtained pure from its salt with oxide of copper (which crystallizes very easily,) by the action of sulphuretted hydrogen. It is very soluble, and may be crystallized. It has a very acid taste, and neutralizes bases, forming crystallizable salts.

6. *Nitrobenzide*, $C_{12}H_4N O_4$. *SYN. Nitrobenzole*.—Formed when benzole is dissolved to saturation in fuming nitric acid, and water added to the hot solution. On cooling, the nitrobenzide falls to the bottom as a heavy oil. It is, at 60° , a yellow liquid, very sweet to the taste, with an odor like that of cinnamon; it boils at 434° , and solidifies at 37° . Its Sp. G. is 1.209. It is insoluble in water, soluble in alcohol and ether. It is formed from 1 eq. benzole and 1 eq. nitric acid, $C_{12}H_4 + N O_5 = H O + C_{12}H_4N O_4$.

By the action of reducing agents, such as sulphuretted hydrogen, nitrobenzide loses the whole of its oxygen, and, taking up 2 eq. of hydrogen, it is transformed into aniline, $C_{12}H_7N$. (See *Aniline*.) Nitrobenzide may be viewed as benzole, $C_{12}H_4$, in which 1 eq. hydrogen is replaced by nitrous acid, $C_{12}H_4 \left\{ \begin{smallmatrix} H \\ N O_2 \end{smallmatrix} \right\}$ while in aniline this eq. of hydrogen is replaced by amide; $C_{12}H_7N = C_{12}H_4 \left\{ \begin{smallmatrix} H \\ N H_2 \end{smallmatrix} \right\}$. By the further action of nitric acid, nitrobenzide is converted into dinitrobenzol, $C_{12}H_4N_2O_6 = C_{12}H_4 \left\{ \begin{smallmatrix} H \\ 2 N O_2 \end{smallmatrix} \right\}$ in which a second eq. of hydrogen is replaced by nitrous acid. This compound, acted on by hydrosulphide of ammonia, yields nitroaniline, a base, the formula of which is $C_{12}H_6N O_4 \left\{ \begin{smallmatrix} H \\ N \end{smallmatrix} \right\}$, corresponding to aniline $C_{12}H_7N$.

7. *Azobenzide*, $C_{12}H_4N$.—This compound is formed when an alcoholic solution of nitrobenzide is distilled with dry hydrate of potash. After the alcohol has distilled, the azobenzide volatilizes, forming large red crystals, fusible at 150° , boiling at 380° . In the production of this compound alcohol takes a part, and there are formed, besides azobenzide, aniline, water, and oxalic acid, which remains combined with the potash: $2 (C_{12}H_4N O_4) + C_4H_4O_6 = C_{12}H_4N + C_{12}H_7N + C_2O_3 + 3 H O$.

8. *Chloride of benzole*, $C_{12}H_4Cl_4$.—Formed when chlorine gas and benzole are exposed to the sun's rays. It is a colorless crystalline solid.

9. *Chlorobenzine*, $C_{12}H_7Cl$. — Obtained by distilling the preceding compound with hydrate of lime, as a colorless oily liquid. Bromine forms with benzole analogous compounds.

10. BENZONE. $C_{12}H_8O$.

One of the products of the distillation of neutral benzoate of lime. When purified from benzole and naphthaline, it is an oily viscid colorless liquid, heavier than water. It differs from 1 eq. of anhydrous benzoic acid by 1 eq. of carbonic acid, $C_{14}H_8O_2 = C_{12}H_8O + CO_2$.

11. HYDROBENZAMIDE. $C_{14}H_{12}N_2$.

When 1 vol. hyduret of benzoyle and 20 vol. of strong aqua ammonia are exposed in an hermetically sealed vessel to a temperature of from 105° to 120° , it is converted after a time into a crystalline mass, which is to be washed with ether. The residue dissolved in alcohol, yields, by spontaneous evaporation, regular crystals of hydrobenzamide. In its formation, 3 eq. hyduret of benzole, and 2 eq. ammonia, produce 1 eq. hydrobenzamide and 6 eq. water: $3(C_{14}H_8O_2) + 2NH_3 = C_{14}H_{12}N_2 + 6H_2O$. If, in preparing this substance, we employ the crude oil of bitter almonds, we obtain a yellow resinous mass, which is a mixture of hydrobenzamide, benzhydramide, azobenzoyle, and azotide of benzoyle, all of them discovered by Laurent.

12. *Benzhydramide* — Is isomeric with hydrobenzamide, but is not converted, like the former, into hyduret of benzoyle and sal ammoniac by the action of hydrochloric acid.

13. *Azobenzoyle*, $C_{14}H_{10}N_2$. — Is much less soluble in alcohol than the preceding. It is derived from benzoyle as follows: $3(C_{14}H_8O_2) + 2NH_3 = C_{14}H_{10}N_2 + 6H_2O$.

14. *Azotide of Benzoyle*, $C_{14}H_8N_3$ — Is quite insoluble in boiling alcohol. It may be derived from anhydrous benzoic acid as follows: $C_{14}H_8O_2 + NH_3 = C_{14}H_8N_3 + 3H_2O$.

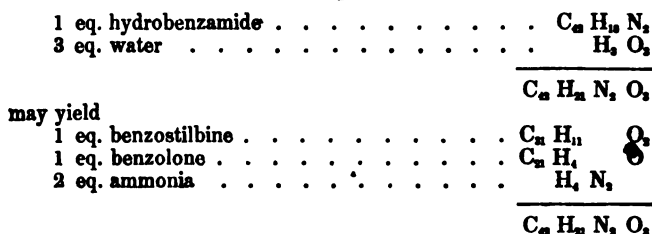
15. BENZOSTILBINE. $C_{24}H_{16}O_2$.

Rochleder has shown that when hydrobenzamide is heated with fused potash, till the mass begins to blacken, three new substances are formed; namely, a yellow oil in very small quantity, and two solid crystalline compounds, benzostilbine and benzolone. Benzostilbine is best obtained by heating only till the mass becomes like gamboge. It is then purified by solution in alcohol, which dissolves it readily when the yellow oil is present. When the oil is destroyed by a little chlorine, the benzostilbine is immediately deposited in small colorless crystals of silvery lustre, which are insoluble in water, sparingly soluble in alcohol, and soluble with a blood-red color in oil of vitriol, from which water precipitates it unchanged.

16. BENZOLONE. $C_{11}H_4O$.

This compound is formed in greatest quantity when the mixture of hydrobenzamide with potash is heated till it becomes blackish brown. The mass is then washed with water, and dissolved in oil of vitriol, to which it gives a splendid red color. The addition of weak alcohol now causes the benzolone to separate in small crystals.

It is obvious that the two preceding compounds contain the whole carbon of the hydrobenzamide, without any of its nitrogen, and they may both be derived from it by the addition of 3 eq. of water and the elimination of 2 eq. ammonia.



It would appear, however, that benzolone is also formed from benzostilbine, which is first produced, and then decomposed by the increased heat. Benzostilbine in fact contains the elements of 2 eq. benzolone, with an excess of carbon and hydrogen, which are partly given off in the form of carburetted hydrogen, and hydrogen, water also being decomposed, the oxygen of which combines with part of the carbon to form carbonic acid, which combines with the potash.

15. AMARINE. $C_{18}H_{18}N_2$.

When the hyduret of benzoyle, or rather, the oil of bitter almonds, is acted on by ammonia and alcohol, there is found an organic base, to which Laurent, its discoverer, has given the name of amarine. Its formula is $C_{18}H_{18}N_2$, and it is, therefore, isomeric, or polymeric, with hydrobenzamide. It is a well-marked base, and we shall return to it as such.

16. LOPHINE. $C_{16}H_{16}N_2$.

When hydrobenzamide is subjected to the action of heat in close vessels, there is formed, among other products, a new organic base, which Laurent has named lophine. It has distinct basic properties, and will be again referred to in the section on organic bases. Its formula is $C_{16}H_{16}N_2$.

The formation of this and of the preceding compound is very interesting, as proving the derivation of bodies having the high atomic weight of the organic bases from bodies of lower equivalents; these bodies, as well as the isomeric hydrobenzamide and benz-

hydramide, being all derived from the hyduret of benzoyle, $C_{14}H_6O_2$. There may be some doubt as to the atomic weight of indifferent bodies, such as hydrobenzamide; but there is hardly any as to that of the bases above mentioned, which are evidently formed by the coalescence of 3 or more eq. of the hyduret of benzoyle, since 1 eq. contains 42 or 46 eq. of carbon, while the hyduret only contains 14 eq. of that element.

17. BENZIMIDE. $C_{22}N H_{11} O_4$.

According to Laurent, this compound is found in the crude oil of bitter almonds. It is crystallizable, and appears to be decomposed by acids into benzoic acid and ammonia. It may be derived from anhydrous bibenzoate of ammonia by the separation of 2 eq. water: $C_{22}H_{10}O_6 + N H_3 = C_{22}H_{11}N O_4 + 2 H O$. But this is not probable. A compound precisely similar is obtained when an alcoholic solution of potash is added to a mixture of hyduret of benzoyle and strong hydrocyanic acid; but this compound yields with acids ammonia and hyduret of benzoyle.

18. BENZOINE. $C_{28}H_{12}O_4$.

Polymeric with hyduret of benzoyle. It is formed when an alcoholic solution of potash, or sulphide or cyanide of potassium, act on the crude oil of bitter almonds, containing hydrocyanic acid. It separates in a congeries of small crystals, insoluble in water, soluble in alcohol. It may be volatilized without change. Sulphuric acid dissolves it with a violet color. Hydrate of potash, melted with it, forms benzoate of potash, with disengagement of hydrogen. It dissolves with a violet color in a hot alcoholic solution of potash, and is converted by boiling with it, into benzoic acid. When its vapor is passed through a red-hot tube, it is converted into hyduret of benzoyle, or at least into an oil smelling like that compound, and passing into benzoic acid on exposure to the air. By the action of chlorine, it loses hydrogen and is converted into benzile, a compound having the composition of the radical benzoyle.

The action of hydrocyanic acid in promoting the formation of benzoine, is not yet explained; but it is certain that from pure hyduret of benzoyle we cannot procure it, while the addition of hydrocyanic acid insures its formation. It is, probably, formed by the simple coalescence of 2 eq. hyduret of benzoyle, and the derivatives of benzoine most likely agree with it in containing 28 eq. of carbon.

19. HYDROBENZOINAMIDE.

Syn. *Benzoinamide*. — Isomeric, or polymeric with hydrobenzamide. It is formed by exposing a mixture of benzoine and ammonia to a moderate heat; and appears as a white tasteless powder, volatile without decomposition.

20. BENZOINAM. $C_{26}N_2H_{21}O_2$.

When a mixture of ammonia, alcohol, and benzoine, is left for several months in a closed bottle, there are formed many products, among which are the preceding compound, benzoinamide, and a new substance, benzoinam, which is with difficulty purified. It forms small white needles, the formula of which is $C_{26}N_2H_{21}O_2$. It is evidently formed by the coalescence of 2 eq. benzoine, (itself produced by the coalescence of 2 eq. hyduret of benzoyle) while ammonia is taken up and water separated. Thus, 2 eq. benzoine = $C_{24}H_{24}O_4$, plus 2 eq. ammonia N_2H_5 , and minus 6 eq. water H_6O_3 , are equal to $C_{26}N_2H_{21}O_2$.

Benzoinam dissolves in acids, and is precipitated by alcalies; it seems, therefore, to have the characters of a weak base.

21. BENZILE. $C_{28}H_{10}O_4$.

SYN. *Benzoyle*. — It is formed by the action of chlorine gas on melted benzoine. When cold the mass is boiled with alcohol, which on cooling deposits benzile in crystals, which are yellow six-sided prisms; insoluble in water, soluble in alcohol and ether, melting at 195° and volatile without decomposition. An alcoholic solution of potash dissolves it with a violet color, and converts it into benzoic acid. Benzile has the composition in 100 parts of the supposed radical benzoyle, but there is good reason to believe its equivalent to be twice as high.

22. BENZILIC ACID. $C_{28}H_{10}O_4 + H O$.

Formed when benzile or benzoine is dissolved in a hot alcoholic solution of potash, and boiled until the violet color at first produced has disappeared, and is no longer restored by a fresh portion of potash. To the boiling solution of benzilate of potash hydrochloric acid is added in excess, and on cooling the benzoic acid is deposited in colorless brilliant crystals, fusible at 248° , not volatile, but yielding, when heated, benzoic acid and purple vapors. Sulphuric acid dissolves it with a bright crimson color. Its formation is explained as follows: 1 eq. of benzile takes up 2 eq. water, one of which is incorporated in the acid; while the other is replaceable by bases; $C_{28}H_{10}O_4 + 2 H O = C_{28}H_{11}O_5 + H O$. Benzilate of potash forms large transparent crystals, soluble in water and alcohol.

23. *Azobenzoide* — $C_{24}H_{22}N_2$? Obtained by adding ammonia to the oil produced when bitter almonds are distilled, per decensum, and dissolving away by means of ether, all other products. A white powder, decomposed by heat. Its formula is doubtful.

24. *Cyanobenzile*. — Formed when an alcoholic solution of benzile is warmed with $\frac{1}{4}$ of its volume of concentrated hydrocyanic acid. It is deposited in large transparent crystals, the composition of which is not yet known.

HYDURET OF SULPHOBENZOYLE. $C_{14}H_8S_2, H.$

One vol. of crude essence of bitter almonds is dissolved in 8 or 10 of alcohol, and gradually mixed with 1 vol. of hydrosulphide of ammonia. After a time, the mixture deposits a fine white powder formed of grains smaller than those of starch, which give to the fingers a very persistent odor of garlic. It is insoluble in water and alcohol. Ether liquefies it, but a few drops of alcohol restore its solid form. It may be considered as the hyduret of a new radical, in which the oxygen of benzoyle has been replaced by sulphur. When heated it melts, and if now allowed to cool, forms first a transparent plastic mass, and afterward a brittle glass. If kept melted for some time, it crystallizes but is now altered.

26. STILBENE. $C_{22}H_{12}.$

When the preceding compound is strongly heated, it gives off a large quantity of sulphuretted hydrogen, and a little of a liquid, apparently bisulphide of carbon. Continuing the heat, there distill over, first a substance crystallizing in pearly scales, stilbene; and later, a compound, crystallizing in needles, called by Laurent, the discoverer, sulphessale. To obtain the stilbene pure, the first crystals are dissolved in boiling alcohol, which leaves undissolved the other body, and on cooling deposits stilbene in tables. These being dissolved in hot ether, form, by slow evaporation, remarkably fine crystals, with the pearly lustre of stilbite: hence the name. It is fusible and volatile, and combines with chlorine and bromine. Nitric acid decomposes it, giving rise to several new products. Chromic acid attacks it with violence, and reproduces hyduret of benzoyle.

Chloride of Stilbene — Is formed when chlorine is passed through melted stilbene. It appears in two isomeric modifications, *a* and *b*, both of which have the formula $C_{22}H_{11}Cl$, but crystallizes in different forms. By the action of a boiling alcoholic solution of potash, each loses 1 eq. of hydrochloric acid (or its elements), and thus they produce two isomeric modifications of a new compound

$C_{22} \left\{ \begin{matrix} H_{11} \\ Cl \end{matrix} \right.$ which Laurent calls chlostilbase; and in which 1 eq. of hydrogen of stilbene is replaced by chlorine. One of these is called chlostilbase *a*, the other chlostilbase *b*. Both are oily liquids, but they are distinguished by the action of bromine, which combines with both, producing again two isomeric compounds, both crystallizable, but in entirely different forms. Their formulæ are, $a \ C_{22} \left\{ \begin{matrix} H_{11} \\ Cl \end{matrix} \right. + Br_2$ and $b \ C_{22} \left\{ \begin{matrix} H_{11} \\ Cl \end{matrix} \right. + Br_2$.

Along with chloride of stilbene is formed another compound, chloride of chlostilbase, analogous to these bromides of chlostilbase. It is a crystallizable solid; formula, $C_{22} \left\{ \begin{matrix} H_{11} \\ Cl \end{matrix} \right. + Cl_2$.

Bromide combines with stilbene, forming the bromide of stilbene, $C_{22}H_{12}, Br_2$, which is a white powder.

When stilbene is boiled with nitric acid, it forms several compounds not yet fully examined. Among these are nitrostilbene, nitrostilbene, and nitrostilbic acid. The latter according to Laurent, is $C_{22}H_{11}NO_{14}$.

27. *Hyduret of Sulphazobenzoyl*, $(C_{14}H_5S_2N_2)H$, or rather $C_{14}H_5S_4N_2$ —Is generally formed along with hyduret of sulphobenzoyl. It seems to be hyduret of benzoyl, in which the 2 eq. oxygen of the benzoyl are replaced partly by sulphur, partly by nitrogen. Besides these compounds, Laurent has described a hydrosulphide of azobenzoyl, with the strange formula $C_{14}H_5N_2S_4$. Ought it not rather to be $C_{14}H_5S_2N_2$, or $C_{28}H_{10}S_4N_2$?

28. NITROBENZOIC ACID. $C_{14}H_5NO_7, HO$.

Formed when nitric acid acts on benzoic acid. It is a crystalline volatile acid, and contains the elements of benzoic acid, in which 1 eq. hyponitric or nitrous acid has been substituted for 1 eq. hydrogen: $C_{14}H_5O_2 - H + NO_4 = C_{14} \left\{ \begin{smallmatrix} H_5 \\ N \end{smallmatrix} O_4 O_2 \right.$;—and the basic water of the benzoic acid unites with the new acid as with the old.

29. BROMIDE OF BENZOLE. $C_{12}H_5Br$.

This compound is formed as a white insoluble powder, when bromine acts on benzole. An alcoholic solution of potash removes hydrobromic acid (or its elements), and causes the separation of a white crystalline body, $C_{12} \left\{ \begin{smallmatrix} H_5 \\ Br_3 \end{smallmatrix} \right.$, which Laurent calls bromobenzinise; and which is formed by substitution of bromine for half the hydrogen of benzole. The bromide of benzole may, therefore, be $C_{12} \left\{ \begin{smallmatrix} H_5 \\ Br_3 \end{smallmatrix} \right. + 3 H Br$.

30. *Hydrocyanate of Benzoin*, $C_{14}N_2H_{12}O_4$ —Is formed as a light crystalline matter, when oil of bitter almonds is mixed with one fourth its volume of dry hydrocyanic acid, and warmed with its own volume of aqua potassæ, Sp. G. 1.25, diluted with six parts of alcohol. It arises from the action of 3 eq. hyduret of benzoyl and 2 eq. hydrocyanic acid: $3(C_{14}H_5O_2) + 2(C_2NH) = C_{44}N_2H_8O_4 + 2 H O$.

31. *Hydrocyanate of Benzile*, $C_{14}H_5O_2 + C_2NH = C_{16}N_2H_8O_2$ —Is formed by direct combination when a hot alcoholic solution of benzile is mixed with an equal bulk of anhydrous hydrocyanic acid. It forms large colorless crystals. Possibly the body called cyanobenzile mentioned above, No. 24, may be identical with this compound.

The above is but a brief and imperfect notice of the numerous compounds which have been obtained from oil of bitter almonds by

the various transformations and decompositions above mentioned. Probably no substance has yielded so rich a harvest of discovery as this remarkable oil, and for our knowledge of the new products we are indebted to Liebig and Wöhler, Mitscherlich, Zinin, Rochleder, but above all, to Laurent, who has discovered by far the greater part of them. Unfortunately, the very able researches of this indefatigable chemist are scattered in several different journals, many of them published at long intervals of time, and have nowhere been collected or exhibited to the world in a connected form. I have not been able to consult nearly all of the original papers, the references to which are very unsatisfactory; and I am consequently compelled to rest satisfied with the imperfect notices which I could find. The above list does not, I believe, contain even the names of several compounds belonging to this series, recently described by Laurent, of which I can procure no distinct account. The reader is therefore, of necessity, referred for the details of these remarkable investigations to the original memoirs which are to be found in the *Annales de Chimie et de Physique*, and the *Journal de Pharmacie*, besides several other French journals.

The study of these compounds has shed great light, and will, in future, shed much more, on the origin of the more complex organic molecules. In several instances, we see 2 or 3 eq. of hyduret of benzoyle coalescing to yield 1 eq. of a new and more complex substance, either with or without a change in the relative proportion of oxygen and hydrogen, and with or without the addition of nitrogen. According to Laurent, compounds exist in which 4, 6, and even 9, eq. of the hyduret have coalesced.

It was mentioned, in a former part of this work, that our power of artificially forming bodies which occur as products of organic life, was limited chiefly to the decomposition or splitting up of complex molecules, such as those of sugar, salicine, uric acid, or fibrine, into less complex molecules.

But, although this is still true of the actual products of organic life which have been imitated in the laboratory, the facts above described, show, that, under certain circumstances, we can, from the less complex molecules, build up more complex ones, so as to produce if not the actual products of organic life, yet substances, entirely analogous to them, and equally complex.

Thus, the artificial bases, amarine, lophine, and benzoïn, have equivalents as high as those of the vegetable alkalies, morphia and quinine; and we have almost demonstrative evidence that these three compounds arise from the reverse process to that which yields urea, formic, oxalic, and salicylic acids. The latter are obtained by processes of oxidation, which tend to split up the more complex molecules into less complex ones: the former are, on the contrary, built up out of the less complex molecules, by processes

of reduction. There are other cases, of recent discovery, which establish the same principle.

Now we know, that the distinguishing feature of vegetable life is the power of reduction possessed by plants, which easily deprive carbonic acid of its oxygen, an operation requiring a prodigious chemical force.

We are, therefore, warranted in concluding that we shall, in time, succeed, by means of the various processes of reduction known to chemists, (and possibly of new methods also), in producing, for example, the vegetable alkalies, morphine, quinine, and strychnine.

This consideration gives to the compounds of the benzoyle series, and their derivatives, a high degree of interest, far surpassing that which would attach to them as a mere list of new compounds, each possessing a distinct composition and distinct properties.

APPENDIX TO BENZOYLE.

1. AMYGDALINE. $C_{20}H_{27}O_{11}$.

Is found in bitter almonds, in the leaves of the cherry laurel, and probably in the kernels of all the bitter species of amygdalus and prunus, as the peach and plum. To obtain it, bitter almonds are pounded and forcibly pressed between warm iron plates to remove the fat oil (oil of almonds). The marc or residue is boiled with alcohol of 94 per cent., and the tinctures distilled off in the water-bath to the consistence of syrup. This liquid, which contains amygdaline and sugar, is diluted with water, mixed with yeast, and set aside. When the fermentation is over, the whole is filtered, and again evaporated to a syrup, which being mixed with a large excess of cold alcohol (of 94 per cent.) deposits the amygdaline as a white crystalline powder. This is pressed in folds of bibulous paper, and finally purified by repeated crystallization from boiling alcohol. It forms crystalline scales very soluble in water, very sparingly soluble in cold alcohol, but more soluble in hot alcohol. It has a bitter taste. When heated it emits an odor like that of May blossom, and leaves a bulky coal.

When distilled with nitric acid, or other oxidizing agents, it is resolved into ammonia, hyduret of benzoyle, benzoic acid, formic acid, and carbonic acid. Caustic alkalies convert it into ammonia and amygdalinic acid: permanganate of potash converts it into cyanate and benzoate of potash.

2. AMYGDALINIC ACID. $C_{18}H_{15}O_{11} + H_2O$.

Prepared by boiling amygdaline with baryta as long as ammonia is given off, and then removing the baryta from the soluble amygdalinate of that base by sulphuric acid. By evaporation it yields a transparent amorphous mass, which has a very pleasant acid taste. Nitric acid, and other oxidizing agents, convert it into

hyduret of benzoyle, with formic and benzoic acid. Its salts are almost all soluble: their formula is $C_{60} H_{24} O_{24} + M O$.

3. DISTILLED WATER OF BITTER ALMONDS.

Expressed bitter almonds are made into a thin cream with water, and this distilled in the heat of a chloride of calcium bath, till a quantity of water has passed over equal in weight to the almonds before being pressed. The distilled water is milky from suspended oil of bitter almonds, and smells both of hyduret of benzoyle and of hydrocyanic acid. When freshly prepared, it contains little more than 1 grain of hydrocyanic acid per ounce; but its strength diminishes by keeping, and as it is difficult to obtain it of uniform strength even when fresh, it is not a good form of administering hydrocyanic acid. It is remarkable, that nitrate of silver does not detect the hydrocyanic acid, unless ammonia is added with the nitrate, and after a time neutralized by nitric acid. It is used in medicine, especially on the Continent, and is poisonous.

4. LAUREL WATER.

Obtained by distilling two parts of fresh leaves of *prunus lauro-cerasus* with water till three parts have passed over. It exactly resembles the preceding water, and is equally uncertain, and equally poisonous.

THEORY OF THE FORMATION OF HYDURET OF BENZOYLE FROM BITTER ALMONDS.

Bitter almonds contain, like sweet almonds, a large quantity of an albuminous or caseous matter, called emulsine or synaptase, along with abundance of a mild fat oil, the oil of almonds, very similar to olive oil. But in addition to these, the bitter almonds contain 4 or 5 per cent. of amygdaline, which is not present in sweet almonds.

Now, if the amygdaline be removed by boiling alcohol, the residue, when distilled with water, does not yield a trace of the volatile oil of bitter almonds. Again, if the residue of the bitter almonds, after the fat oil has been pressed out, be heated to such a point as to coagulate the emulsine, before water is added, the distillation also yields no volatile oil, even although the amygdaline be present.

These facts prove that the production of the volatile oil of bitter almonds depends on the presence, first, of amygdaline; secondly, of soluble emulsine; and that it is the result of the mutual action of these bodies on each other. This is further demonstrated by the fact, that if amygdaline be placed in contact with the emulsine or synaptase of sweet almonds, and water, distillation of the mixture now yields the oil abundantly.

When the solution of 10 parts of amygdaline in 100 of water is added to a solution of 1 part of synaptase in 10 of water, mutual decomposition at once takes place: the liquid acquires the odor of hyduret of benzoyle, and of hydrocyanic acid, and when distilled, yields the crude oil of bitter almonds, which is a mixture of these two compounds. The residue of the distillation contains sugar in such quantity, that it is probable the elements of the synaptase have contributed to form it; and when this sugar is destroyed by fermentation, a fixed acid is found. If the synaptase has been coagulated, it has not the slightest action on amygdaline.

When the expressed bitter almonds are moistened with water, the very same reaction occurs; and if enough water be present to dissolve the oil as it is formed, the whole amygdaline disappears in a short time. But if the expressed almonds be thrown into boiling water, the synaptase coagulates, and can then produce no change in the amygdaline. To obtain the full proportion of oil, 1 part of expressed almonds should be macerated for 24 hours with 20 parts of water at about 102° , and then distilled.

100 parts of amygdaline produce 47 of crude oil, and these 47 parts of crude oil contain almost exactly 6 of anhydrous hydrocyanic acid; so that 17 grains of amygdaline dissolved in 1 oz. of emulsion of sweet almonds, yields a mixture containing 1 grain of dry hydrocyanic acid, and consequently of the same strength as the distilled water professes to be. This mixture has, besides, the advantage of containing the hyduret of benzoyle present in the distilled water, to which is perhaps owing the superiority of the distilled water of bitter almonds on laurel leaves over mere diluted hydrocyanic acid, a superiority, which, according to the Continental physicians, is very decided and obvious. The above simple recipe, given by Liebig and Wöhler, is admirably adapted for extemporaneous use, and the mixture ought never to be made in a larger quantity at a time, as, like the distilled water, it alters by keeping.

In the above remarkable decomposition, we have a very beautiful example of a metamorphosis in which the elements of two bodies take a share; but as the whole of the products are not yet exactly known, and even the composition of the emulsine or synaptase is uncertain, we cannot explain the whole change with precision. We know, however, that from 1 eq. amygdaline, $C_{20}N H_{27} O_{22}$, the following compounds may be derived:—

1 eq. hydrocyanic acid	$C_2 N H$
2 eq. hyduret of benzoyle	$C_{12} H_{12} O_4$
$\frac{1}{2}$ eq. sugar	$C_6 H_{12} O_6$
$\frac{1}{2}$ eq. formic acid	$C_1 H_2 O_2$
7 eq. water	$H_7 O_7$
1 eq. amygdaline	$C_{20} N H_{27} O_{22}$

Also, 1 eq. amygdalinic acid, $C_{40}H_{28}O_{24}$, may yield:

3 eq. formic acid	$C_3H_2O_3$
2 eq. hyduret of benzoyle	$C_{22}H_{12}O_4$
$\frac{1}{2}$ eq. sugar	$C_6H_{12}O_6$
6 eq. water	H_2O

1 eq. amygdalinic acid $C_{40}H_{28}O_{24}$

Now, we can trace all these products among the results of this transformation; and, it is probable, not only that there is more sugar than can be accounted for by the amygdaline, but also that other products, not yet known, are formed; as, for example, the fixed acid above alluded to. The emulsine or synaptase, which produces this remarkable change is amygdaline, in which it itself participates, contains nitrogen, is soluble in water, coagulable by heat, and in short very analogous both to albumen and caseine, along with which we shall again notice it. In the almond it appears to be accompanied by albumen.

We have seen, above, that the assumption of the existence of the radical benzoyle brings a number of compounds into a more easily understood form, and very materially aids the memory by enabling us to classify these compounds as analogous to others better known. Other views may be taken of this series of compounds: for example, according to Dumas, hyduret of benzoyle may be represented as a compound of benzoic acid with a carbo-hydrogen, $2 C_{14}H_5O_2 + (C_{14}H_5)H_2$; benzoic acid being the teroxide and the carbo-hydrogen the terhyduret of the body, $C_{14}H_5$: for $2 (C_{14}H_5)O_3 + (C_{14}H_5)H_2 = C_{42}H_{16}O_6 = 3 (C_{14}H_5O_2) = 3 BzH$. The same view might be extended to some of the other compounds of benzoyle, but it is complex, and cannot well be applied to benzamide, hydrobenzamide, and several others. Again, according to Mitscherlich, benzoic acid is $C_{18}H_8 + 2 CO_2$; that is, benzole plus 2 eq. carbonic acid; while a dry benzoate would contain, united to the base, the hypothetical body benzide, $C_{18}H_8$, and the equally hypothetical anhydrous oxalic acid, C_2O_3 . These views appear both to be in all respects inferior to that which we have adopted, and which must be retained, until a better shall be proposed. If I understand rightly some expressions in a recent paper by Laurent, that chemist considers hyduret of benzoyle, $C_{14}H_5O_{21}$, as the oxide of a radical benzene; but it does not appear, whether it is $(C_{14}H_5) + O_2$ or $(C_{14}H_5O) + O$. The term oxide of benzene, however, may be applied to one of the isomeric modifications of the hyduret.

XIV. SALICYLE. $C_{11}H_6O_4 = Sa$.

This is the hypothetical radical of a remarkable series of compounds; and, as such, belongs to the same group as benzoyle. Its most interesting compound is the hyduret of salicyle, which we shall therefore first consider.

1. HYDURET OF SALICYLE. $C_{11}H_8O_4$, $H = Sa H$.

Syn. Salicylous Acid. — This compound is found as the chief ingredient in the essence of meadowsweet, that is, the essential oil obtained by distilling the flowers of *spiraea ulmaria* with water. It is probable that, like the essence of bitter almonds, it is formed by the metamorphosis of a compound or compounds present in the flowers. The crude essence is distilled with aqua potassæ, which combines with the hyduret, and an oil distils over which seems to be a carbo-hydrogen. The salt of potash being now redistilled with a slight excess of dilute sulphuric acid, yields the pure hyduret of salicyle.

It may also be obtained by distilling one part of salicine, one part of bichromate of potash, two and a half of oil of vitriol, and twenty of water, together. The salicine is dissolved in part of the water, and the acid diluted with the rest. The mixture is then made in a retort, and after the effervescence which takes place is over, the whole is distilled, and yields the hyduret, to the amount of one-fourth of the salicine employed.

Hyduret of salicyle is an oily colorless liquid, having a fragrant aromatic odor and a burning taste. Its Sp. G. is 1.1731, and it boils at about 380° . With chlorine and bromine it forms new compounds. With bases it forms salicylurets, water being separated: $H Sa + M O = H O + M Sa$, so that it has the characters of an acid.

Salicyluret of Ammonium, $Sa, N H_4$. — Is formed when concentrated ammonia is poured upon hyduret of salicyle. It is a yellow solid, having a faint odor of roses. When moist, this salt is decomposed spontaneously, becoming black, and giving off ammonia and an odor like that of roses. With dry ammoniacal gas, hyduret of salicyle forms the compound $3 Sa H + 2 N H_3$.

Salicylimide, $C_{11}N, H_{11}O_4$. — Is formed when caustic ammonia is added, drop by drop, to a solution of 1 vol. hyduret of salicyle in 3 vol. alcohol, and the small yellow crystals which first formed are dissolved by a gentle heat. On standing, salicylimide appears in the form of golden yellow brilliant prisms. It is formed from 3 eq. hyduret of salicyle and 2 eq. of ammonia, by the separation of 6 eq. water, $3 (C_{11}H_8O_4) + 2 N H_3 - 6 H O = C_{11}N, H_{11}O_4$. As it is no longer soluble in the liquid from which it was first deposited, it is probable that the yellow salt first formed, which dissolved in the alcohol by aid of a gentle heat was salicyluret of ammonium, which, by excess of ammonia, was converted into salicylimide.

The salts of the hyduret of salicyle or hydrosalicylic acid, are constituted, for the most part, according to the formula $Sa M$. The potassium salt $Sa K$, when exposed to the air in a moist state, becomes first green, then black. When the change is complete, water dissolves acetate of potash, and leaves a black matter,

melanic acid, $C_{10}H_4O_5$. 1 eq. of salicyluret of potassium, 2 eq. water, and 3 eq. oxygen, contain the elements of 1 eq. acetate of potash, and 1 eq. melanic acid: $C_{14}H_2O_4, K + 2H_2O + O_2 = C_{10}H_4O_5, K + C_{10}H_4O_5$. Melanic acid combines with bases.

Ettling and Stenhouse have shown that when the salicyluret of copper, $Cu Sa = C_{14}H_2O_4 + Cu$, and the benzoate of copper, $Cu O, C_{14}H_2O_4$, which is isomeric with it, are distilled, several new products are formed. Among these are salicylic acid and two crystalline neutral compounds.

Parasalicyle—Is a product of the action of heat on salicyluret (salicylite) of copper. Its formula is $C_{14}H_2O_4$, and it has the composition of anhydrous benzoic acid, or of salicylous acid, (hyduret of salicyle viewed as an oxygen acid), as it exists in its salts. The copper salt from which it is formed may be represented either as $C_{14}H_2O_4 + Cu$, or as $Cu O, C_{14}H_2O_4$. Parasalicyle is fusible and volatile, and only attacked by strong acids.

When benzoate of copper is distilled, there is formed, besides salicylic acid, a neutral volatile crystalline compound, which contains 1 eq. oxygen less than parasalicyle, and the formula of which is consequently $C_{14}H_2O_3$. It is therefore isomeric with benzile, and has the composition of the radical benzoyle. Indeed, as it yields benzoic acid when acted on by potash, while benzile yields benzoic acid, it may very probably be that radical. It has not, however, been named by Ettling, who discovered it.

2. SALICYLIC ACID. $(C_{14}H_2O_4)O, HO = Sa O, HO = Sa O, H$.

Formed when hyduret of salicyle is heated with hydrate of potash till the mass loses its brown color. Hydrogen is given off, and salicylate of potash is formed. Hydrochloric acid, added to the solution of this salt, causes the deposition of crystals of salicylic acid.

The same acid is formed when coumarine, the stearoptene or camphor of the tonka bean, is acted on by caustic potash. Moreover the essential oil of wintergreen, or gaultheria procumbens, appears, by the researches of Cahours and Gerhard, to be the salicylate of oxide of methyle. The acid, therefore, is most readily obtained, by gently heating this oil with a slight excess of potash, and afterward adding an acid, when the salicylic acid, being very sparingly soluble, is deposited. It is easily purified by recrystallization, and sometimes forms crystals one or two inches in length.

Salicylic acid crystallizes in tufts of slender prisms, very like benzoic acid. It may be sublimed without decomposition. The formation of this acid from hyduret of salicyle is very simple: $C_{14}H_2O_4, H + KO, HO = C_{14}H_2O_4, KO + H_2$. When the salicylate of potash is decomposed by an acid, the salicylic acid takes up 1 eq. of basic water, and separates as $C_{14}H_2O_4, H O, H O$.

$C_{14} H_8 O_6, H$. The decompositions of this acid are very interesting, connecting it with several other series of organic compounds.

When it is acted on by nitric acid, it is first converted into indigotic acid, or anilic acid, $C_{14} H_8 N O_6, H O$, along with other products; and by the continued action of nitric acid, there is finally produced the remarkable bitter acid, called carbazotic, or nitropicric acid, $C_{12} H_2 N_2 O_{11}, H O$. Both these acids are formed from indigo by the action of nitric acid.

When salicylic acid is distilled with caustic baryta, it yields carbonate of baryta, and a heavy oily liquid, which is the acid known as carbohic acid, (*Runge*), and hydrate of phenyle (*Laurent*), the formula of which is $C_{12} H_2 O_2 = C_{12} H_2, O, H O$. The production of carbohic acid from salicylic acid is easily understood: it is, in fact, analogous to that of benzine from benzoic acid: $C_{14} H_8 O_6, H O + 2 Ba O = 2 (Ba O, C O_2) + C_{12} H_2 O_2$. As the action with baryta is so violent as to destroy a great part of the acid, it is found better to heat rapidly salicylic acid mixed with powdered glass, when it is resolved into carbohic and carbonic acids.

Now it is very remarkable, that carbohic acid, which is one of the chief ingredients of the oil of coal tar, a product, therefore, of the destructive distillation, is also converted by the action of nitric acid into nitropicric acid. This would indicate that when salicylic acid is acted on by nitric acid, it yields, first, some compound containing the same radical as carbohic and nitropicric acid, and that this is further oxidized into the latter acid. We shall hereafter see that the probable radical of carbohic acid is *phène*, $C_{12} O_2$, from which, by substitution and oxidation, carbohic and nitropicric acids, and a whole series of compounds, may be formed.

On the whole, from its relation to hyduret of salicyle and to salicine (from which it may also be formed by the action of caustic potash), from its analogy in formation, constitution, and properties to benzoic acid, from its occurrence in nature in the first compound of methyle not artificially produced, and from its ready convertibility into indigotic acid, carbohic acid, and nitropicric acid, salicylic acid is a compound of very great interest.

The salts of salicylic acid have the general formula $C_{14} H_8 O_6, M O$ or $C_{14} H_8 O_6, M$. The salicylate of oxide of methyle, $C_2 H_2 O + C_{14} H_8 O_6$, occurs in the essential oil of *gaultheria procumbens*, and is much used in perfumery. It gives rise to a number of remarkable products, when subjected to the action of nitric acid, chlorine, bromine, alcalies, &c.; but all these things will be treated of in their proper places.

3. CHLOROSALICYLIC ACID. $C_{14} H_8 \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right.$ or $C_{14} H_8 O_2, Cl$.

When dry chlorine is made to act on dry hyduret of salicyle, this compound is formed, along with hydrochloric acid; it crystallizes readily, and may be sublimed unchanged. Its formation

is entirely analogous to that of chloride of benzoyle, and it might be viewed as chloride of salicyle, $C_{14}H_5O_4, Cl = Sa\ Cl$. But its properties are those of an acid, and hence we are compelled to consider it as salicylic acid, $C_{14}H_5O_4$, in which 1 eq. oxygen has been replaced by 1 eq. chlorine, the type remaining unchanged. Hence, after this substitution, it is still an acid, and its true formula is $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ Cl \end{smallmatrix} \right.$, an acid of the type of anhydrous salicylic acid.

With ammonia it forms a new compound, chlorosalicylimide. As in the action of ammonia on hyduret of salicyle, so in this case, 2 eq. ammonia act on 3 of the acid, and 6 of water are separated. The formula of chlorosalicylimide, which is a yellow, insoluble solid, is $C_{42}H_{15}N_3Cl_3O_6$; for $3(C_{14}H_5ClO_4) + 2N_3H_3 = 6H_2O + C_{42}H_{15}Cl_3N_3O_6$. It is, in fact, salicylimide in which 3 eq. chlorine have been substituted for 3 eq. hydrogen.

With bromine and iodine, hyduret of salicyle yields the two analogous compounds, bromosalicylic acid, and iodosalicylic acid; $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ Br \end{smallmatrix} \right.$, and $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ I \end{smallmatrix} \right.$.

4. NITROSALICYLIC ACID. $C_{14}H_5N O_6 = C_{14}H_5N O_5, H O$.

Syn. Anilic Acid. Indigotic Acid.—This acid is formed by the action of nitric acid on hyduret of salicyle, or still better, on salicylic acid. It forms yellow prisms, and with bases yields yellow detonating salts. Ammonia colors it blood-red, and perchloride of iron cherry-red. It would appear, according to the above formula, derived from the analysis of Piria, to be salicylic acid, in which 1 eq. nitrous (hyponitric) acid is substituted for 1 eq. hydrogen. But its characters, and those of its salts, are such as to convince us that it is identical with indigotic, or anilic acid; under which names we shall have again to treat of it.

APPENDIX TO SALICYLE.

5. SALICINE. $C_{28}H_{18}O_{11} = C_{12}H_{10}O_6 + C_{14}H_8O_5$.

This compound occurs in the bark of all such willows as are bitter, such as *Salix helix*, *S. amygdalina*, &c. It is extracted by boiling with water, decolorizing the decoction with litharge, removing the lead dissolved by sulphuric acid and sulphide of barium, and evaporating to a syrup. The salicine crystallizes on standing, in fine scales of a silky lustre, which have a very pure bitter taste, and are highly febrifuge. It is neutral, soluble in water and alcohol, insoluble in ether. Oil of vitriol colors it blood-red. Distilled with bichromate of potash and sulphuric acid, it yields formic and carbonic acids, hyduret of salicyle, and a resinous matter.

6. SALIGENINE. $C_{14}H_5O_4$.

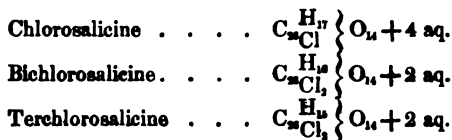
The recent researches of Piria have greatly extended our knowledge of salicine. The formula above given for salicine is deduced

from his analyses, and he has shown that by contact with synaptase, salicine is decomposed, being resolved into sugar. $C_{12}H_{18}O_{10}$, (which takes up 4 eq. of water and appears as grape sugar, $C_{12}H_{22}O_{14}$) and a new body, saligenine, $C_{14}H_8O_4$. When the metamorphosis is complete, which, with 200 parts of water, and 3 parts of synaptase for 50 of salicine, and a temperature of 106° , taken place in 24 hours, most of the saligenine separates in crystals, being very sparingly soluble in cold water, and the rest is obtained by agitating the solution with ether, which dissolves the saligenine. The aqueous liquid is now found to contain only grape sugar, and the residue of the synaptase.

Saligenine melts at 180° , and forms on cooling a crystalline mass. It appears to form a combination with potash, but when it is heated with that alkali, hydrogen is disengaged and salicylic acid is formed. Several oxidizing agents convert saligenine into hyduret of salicylic, from which it differs only by containing 2 eq. of hydrogen more. Aqueous solutions of perchloride of iron and of salts of peroxide of iron strike an indigo blue with saligenine; but this color is not formed when alcoholic or etherial solutions are used. The blue compound has not been separated. When heated to a certain point, or boiled with acids, saligenine is converted into saliretine, a body which is also obtained when salicine is boiled with dilute acids, and which is no doubt in this latter case derived from the saligenine contained in the salicine. Saliretine will be described presently.

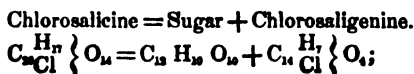
As it appears certain from the experiments of Piria that salicine is composed of saligenine and sugar, the products of various reactions on salicine will be generally those on a mixture of saligenine and sugar. It will therefore be better to describe in connection the substances produced from saligenine, and those formed from salicine.

By the action of chlorine on salicine, there are formed three compounds analogous to salicine, in which 1, 2, and 3 eq. of hydrogen are replaced by chlorine. These are:

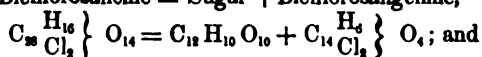


These compounds are all crystallized, and all of them, like salicine, are decomposed by fermentation in contact with synaptase into sugar and a body derived from saligenine.

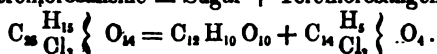
Thus we have:



Bichlorosalicine = Sugar + Bichlorosaligenine,



Terchlorosalicine = Sugar + Terchlorosaligenine,

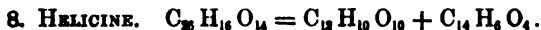


Chlorosaligenine forms very fine crystals, and is singularly like saligenine in its outward characters. It colors oil of vitriol, however, green, whereas saligenine colors it red, as does also salicine. The two other compounds are obtained with much greater difficulty by the action of synaptase or bichlorosalicine and terchlorosalicine, owing to the very sparing solubility of these compounds. But their existence has been established.

7. SALIRETINE.

When saligenine is boiled with diluted acid, or heated beyond its melting point, it is changed into a resinous substance, which differs from saligenine only by 2 eq. water. Its empirical formula is $C_{14} H_6 O_2$, and therefore it is isomeric or polymeric with hyduret of benzoyl.

It appears that chlorosaligenine, bichlorosaligenine, and terchlorosaligenine also yield resins when boiled with acids, and these resins are in all probability derived from saliretine, and composed of $C_{14} \left\{ \begin{array}{l} H_2 \\ Cl \end{array} \right\} O_2$, $C_{14} \left\{ \begin{array}{l} H_4 \\ Cl_2 \end{array} \right\} O_2$, $C_{14} \left\{ \begin{array}{l} H_2 \\ Cl_3 \end{array} \right\} O_2$. If so, they will be named chlorosaliretine, bichlorosaliretine, and terchlorosaliretine.



This compound is formed when salicine is acted on by diluted nitric acid. When pure it forms small white needles, which contain, in addition to twice the above formula, 3 eq. water of crystallization. Helicine contains the elements of sugar and hyduret of salicyl, and is actually resolved into them by synaptase, and in other ways. It is no doubt formed by the oxidation of the saligenine, producing hyduret of salicyl, which then unites with the sugar to form helicine.

Helicine, when heated to 347° , is converted into an insoluble resinous mass.

When the oxidation of salicine is carried farther, the sugar is destroyed, and yields formic and carbonic acids; but when the oxidation is insufficient to form helicine, there is produced a body, helicoidine, the empirical formula of which is $C_{28} H_{24} O_{20} + 3 \text{ eq.} = 2 \text{ eq. sugar, } C_{14} H_{20} O_{10}; 1 \text{ eq. hyduret of salicyl, } C_{14} H_6 O_4; \text{ and } 1 \text{ eq. saligenine, } C_{14} H_6 O_4$.

By the action of chlorine, helicine yields chlorohelicine $C_{28} \left\{ \begin{array}{l} H_{15} \\ Cl \end{array} \right\} O_{14}$, which is formed of sugar and chloride of salicyl, C_{28}

$H_{10} O_{10} + C_{14} \begin{matrix} H_2 \\ Cl \end{matrix} \} O_4$. With bromine it yields a similar compound.

Rutiline is the name given to the red compound formed by the action of oil of vitriol on salicine. When pure it is of a deep reddish brown color; acids change it to a bright red, alkalies to a deep violet.

9. PHLORIDZINE. $C_{22} H_{22} O_{24} = C_{22} H_{22} O_{18} + 6 H O ?$

This is a substance, very analogous to salicine, which occurs in the bark of the roots of the apple, pear, plum, &c. It is extracted in the same way as salicine, and resembles it much; forming small scales, soluble in hot water, and in alcohol, very bitter, and powerfully febrifuge. When boiled with dilute sulphuric acid, it yields a resinous compound, phloretine, analogous to saliretine, along with grape sugar. Phloretine is $C_{20} H_{16} O_{10} = C_{20} N_{14} O_8$, $H O ?$ and $C_{20} H_{16} O_{10} + C_{12} H_{14} O_{14} = C_{22} H_{22} O_{24}$. According to Stas, however, phloretine is $C_8 H_2 O_8$, or double or quadruple of this. The compound of phloretine with oxide of lead, he found to be $C_{12} H_4 O_8$, $2 Pb O$; which would indicate for hydrated phloretine, $C_{12} H_4 O_8$, $2 H O = C_{12} H_6 O_4$, $H O = C_{12} H_7 O_4 ?$

By the action of nitric acid on phloridzine, there is formed a puce-colored acid, nitro-phloretic acid, which, according to Piria, is $C_{20} H_{12} N O_{16}$; according to Stas, $C_{24} H_{10} N O_{18}$.

Phloridzine, $C_{22} H_{22} N_2 O_{22} ?$ —When moist phloridzine is exposed to air and ammonia, it is transformed into a deep-red compound, which dissolves in ammonia and may be precipitated by acids. It is equal to phloridzine, plus 8 eq. oxygen and 2 eq. ammonia. When dissolved in ammonia, and dried in vacuo, it leaves a purple mass, with coppery lustre, which communicates to water a splendid blue color. This is a compound of phloridzine and 1 eq. ammonia. The formation of this blue pigment is a very good example of that kind of eremacausis with the aid of ammonia, by which indigo, litmus, orchil, &c., are produced from colorless bodies.

When salicine was supposed to be $C_{22} H_{22} O_{20}$, phloridzine appeared to differ from it by only 2 eq. oxygen; but as that formula for salicine, according to Piria, is erroneous, it is most probable that the formula of phloridzine will require to be changed. It is, therefore, marked as doubtful, along with its derivatives.

XV. CINNAMYLE. $C_{12} H_8 O_2 = Ci$.

The radical of essence of cinnamon, but unknown in a separate form.

1. HYDRET OF CINNAMYLE. $Ci H = C_{12} H_8 O_2 = C_{12} H_8 O_2, H$.

This is the purified essence or oil of cinnamon. The oil of commerce contains, besides cinnamic acid and two resins, all of

which have been produced from the original oil, $C_{20}H_{11}O_2$, by the additions to 3 eq. of it, of 8 eq. oxygen. $3(C_{20}H_{11}O_2) + O_8 = C_{18}H_8O_4$ (cinnamic acid) + $C_{12}H_5O$ (a resin); + $C_{20}H_{11}O_4$ (another resin), + 5 H O. With less oxygen, hyduret of cinnamyle, $C_{18}H_8O_2$, is formed, along with the resins, so that the oil of commerce contains, besides the original oil, all the compounds above mentioned.

The hyduret of cinnamyle, $C_{18}H_8O_2$, is a fragrant oil. It forms with nitric acid a crystalline compound, $C_{18}H_8 + N O_4$, which when mixed with water is resolved into its constituents, hyduret of cinnamyle and nitric acid. When the hyduret is exposed to the air, it absorbs oxygen, producing cinnamic acid, $C_{18}H_8O_4 = C_{18}H_8O_2 + H O$.

The fresh oil of cinnamon is, as has been stated, $C_{20}H_{11}O_2$. With 6 eq. oxygen from the air, it yields hyduret of cinnamyle and the two resins: with 2 eq. more, the hyduret passes into cinnamic acid. With oil of vitriol, 3 eq. of the fresh oil = $C_{20}H_{11}O_2$, lose 3 eq. water, and form two resins, one = $C_{20}H_{11}O$; the other = $C_{20}H_{11}O_2$. With hydrochloric acid, it yields an oil and two resins; one, $C_{20}H_{11}O$; the other $C_{14}H_5O$.

2. CINNAMIC ACID. $C_{18}H_8O_4 + H O = C_{18}H_8O_2 + H O$.

Formed by exposing oil of cinnamon to the air. It is most easily obtained by dissolving the oil of balsam of Peru in an alcoholic solution of potash, evaporating to dryness, dissolving in hot water, and adding to the solution of cinnamate of potash an excess of hydrochloric acid. It crystallizes very readily, and may be sublimed. By the action of nitric acid, cinnamic acid is converted into hyduret of benzoyl, and into an acid very similar to benzoic acid, if not identical with it. When cinnamic acid is added to cold nitric acid, it forms an acid, $C_{18}H_7N O_5 = C_{18}H_8O_4 - H + N O_4$; that is, cinnamic acid, in which 1 eq. of nitrous acid is substituted for 1 of hydrogen; $C_{18} \begin{Bmatrix} H_8 \\ NO_4 \end{Bmatrix} O_4 + H O$. This is nitrocinnamic acid. Its salts detonate when heated. With oxide of ethyle, it forms a crystallizable ether, $Ae O, C_{18}H_8N O_7$. When oil of cinnamon is mixed with fuming sulphuric acid, there is formed, according to Herzog, a new acid, sulphocinnamic acid, the formula of which is $C_{18}H_8O_2 + 2 S O_2 + 2 H O = C_{18}H_8O_{10}S_2$. It is bibasic, and almost all its salts are soluble.

When oil of cinnamon is acted on by nitric acid with the aid of heat, it yields benzoic and nitrobenzoic acids. By the action of chlorine, oil of cinnamon is converted into several new products, one of which is chlorocinnose, $C_{18} \begin{Bmatrix} H_4 \\ Cl_4 \end{Bmatrix} O_4$. It is hyduret of cinnamyle in which 4 eq. of chlorine are substituted for 4 eq. of hydrogen.

Balsam of Peru contains compounds connected with cinnamyle. The principal is an oil, cinnameine, which, when boiled with alkalies, yields cinnamic acid and a neutral oily body, peravine, $C_{18}H_{18}O_2$: Cinnameine, heated with dry potash, yields hydrogen gas and pure cinnamate of potash. When exposed to cold, cinnameine deposits crystals, which have the same composition as hyduret of cinnamyle, and are therefore an isomeric modification, analogous to benzoine.

According to Richter, balsam of Peru contains two distinct oils, myroxiline, insoluble in alcohol, and myriospermine, soluble in alcohol. With an alcoholic solution of potash, myriospermine yields an acid resembling cinnamic acid, but different from it, myriospermic acid.

BALSAM OF TOLU.

Tolene; Benzoene.

According to Deville, balsam of tolu contains benzoic acid, and a body isomeric with hyduret of benzoyle; also, cinnameine, and a liquid carbo-hydrogen, tolene, the formula of which is $C_{14}H_{18}$; besides several resins, and another liquid, carbo-hydrogen, analogous to benzole, the name given to which is benzoene, and its formula $C_{14}H_8$. It boils at 226° , and its Sp. G. is 0.87 at 65° F. When acted on by nitric acid, benzoene yields two new compounds, in which the hydrogen is partly replaced by nitrous acid. These are, 1st, protonitrobenzoene, $C_{14}H_7NO_4$, which is liquid; and, 2d, binitrobenzoene, $C_{14}H_6N_2O_8$, which is a crystalline solid. By the action of chlorine on benzoene, Deville has also obtained a series of compounds in which the hydrogen is replaced by chlorine; these compounds, however, chiefly occur in combination with hydrochloric acid. Benzoene dissolves in fuming sulphuric acid, and forms a crystalline mass of sulphobenzoenic acid, the composition of which, according to Deville, is $C_{14}H_7S_2O_8$; that is, 1 eq. of hydrogen seems to be replaced by 1 eq. hyposulphuric acid. Perhaps a better name for this acid would be hyposulphobenzoenic acid. It is analogous to the sulphonaphthalic or hyposulphonaphthalic acid.

XVI. GUAIACYLE. $C_{14}H_8O_4$?

Hyduret of Guaiacyle. $C_{14}H_8O_4 = C_{14}H_7O_4 + H$?

When the resin or gum resin, called guaiacum, is distilled, there is obtained, among other products, a colorless oily liquid, which has acid properties. According to Deville, it is analogous to the hyduret of salicyle, which is also an acid, and is sometimes called salicylous acid. Indeed, Sobrero, who first obtained the acid from guaiacum, called it pyroguaiacic acid. If viewed as a hydrogen acid, it will be the hyduret of guaiacyle, $C_{14}H_7O_4 + H$, and this

agrees with the formula deduced from analysis $C_{14}H_8O_4$, which is that of saligenine. The acid corresponding to salicylic acid has not been formed, but will probably hereafter be obtained. Its formula will be $C_{14}H_8O_6 = C_{14}H_7O_5, H O$. But Thierry has obtained another acid, which he calls guaiacic acid, the formula of which is $C_{12}H_8O_6 = C_{12}H_7O_5, H O$. Deville has also described another oil, which is neutral, and seems to be derived from this last acid, as benzole from benzoic acid. Its formula is $C_{12}H_8O_5$; and it is derived from the acid $C_{12}H_8O_6$ by the separation of 2 eq. carbonic acid; for $C_{12}H_8O_6 - 2 C O_2 = C_{12}H_8O_4$. This neutral oil has been called guaiacène.

In the preceding pages we have considered a large number of compound radicals, constituting chiefly the group of radicals analogous in their relations to chlorine; namely, cyanogen; ferrocyanogen and its numerous congeners; sulphocyanogen; and mellone. We have only described one radical, amide, which has a tendency to produce basic compounds, such as ammonia, ammonium, and the platinized bases; and one, carbonic oxide or oxalyle, the chief tendency of which is to form acid compounds, such as oxalic, carbonic, rhodizonic, croconic, and mellitic acids. Finally, we have studied three; namely, benzoyle, salicyle and cinnamyle, whose characteristic is to form essences or fragrant volatile compounds, with hydrogen, acids with oxygen, and peculiar compounds with chlorine, iodine, &c. This last group would appear to have a strong tendency to form acid compounds: for not only is an acid formed by the union of salicyle and oxygen, but the hyduret of salicyle is a decided acid, and may be represented as salicylous acid, $C_{14}H_8O_5, H O$, isomeric with benzoic acid, instead of hyduret of salicyle, $C_{14}H_8O_4, H$. Further, the chloride, bromide, and iodide of salicyle, although they contain salicyle, plus those elements, are all strong acids, and appear to be in fact anhydrous salicylic acid, with 1 eq. of chlorine, &c., substituted for 1 eq. of oxygen. It is evident that this group of radicals, so well characterized by their hydrogen compounds, does not correspond exactly to any simple radical, but has characters common to different groups of elementary radicals, being, however, analogous in more points to carbon, sulphur, and phosphorus, than to any other elements. In studying the decomposition of the compounds of salicyle, we have met with the very remarkable fact of the production from that radical of a series of compounds: namely, anilic acid, nitropicric acid, carbolic acid, &c., probably derivatives of a totally different radical, phenyle; which radical is also met with in numerous other decompositions, and especially in the decomposition of indigo by nitric acid, by alcalies, and by heat, and in the destructive distillation of coal. This is an important consideration, as every day's experience tends to identify with each other the products of decomposition of different and apparently quite

unconnected organic compounds, even in cases where these products have been described as different. Another very important fact which has come under our notice is the occurrence of salicylate of oxide of methyle as the chief ingredient in the oil of gaultheria. Not only is the occurrence of salicylic acid interesting, since this acid was only known before as an artificial product, but the existence, in this oil, of oxide of methyle, hitherto only known as a product of destructive distillation, goes far to confirm the theory which admits this radical, methyle, and others similar to it. All the properties of the oil of gaultheria entirely agree with the doctrine of its containing two radicals, methyle and salicylc; the former oxidized as a base; the latter, also oxidized, as an acid. It is remarkable, however, that even this compound plays the part of an acid, and forms crystalline salts with the alcalies into which it enters unchanged. This is so well marked a character that the oil has been called gaultheric acid, and the salts gaultherates.

We now proceed to consider that group of radicals to which methyle belongs, and which are analogous, in their relations, to metals, more than to any other class of elements; forming, like metals, bases with oxygen. This group contains Ethyle, Methyle, Amyle, Glyceryle, Cetyle, Allyle, and Cacodyle; besides several radicals, derived from the decomposition of these; as, Acetylc from Ethyle, Formyle from Methyle, and Acrylc from Glyceryle. These latter, however, belong to that group which are analogous to the combustible metalloids, and form acids with oxygen, instead of bases, like the radicals from which they are derived, and in connection with which they shall be described.

XVII. ETHYLE. $C_2H_4 = Ae.$

Unknown hitherto in a separate form; but very well known as anhydrous oxide, or ether, and hydrated oxide, or alcohol. These compounds have not yet been found as natural products of vegetable life, although it is probable that the fragrance of certain fruits, such as pine-apples, melons, apples, is derived from compounds of ethyle. The compounds of ethyle, especially alcohol, are, however, very abundantly produced by the fermentation of saccharine vegetable juices, such as that of the grape. The alcoholic or vinous fermentation of sugar is a metamorphosis, induced in the sugar by contact with yeast or ferment, which is gluten or fibrine in a state of decomposition. In this metamorphosis, the particles of the ferment only act in communicating mechanical motion to those of the sugar: they do not join the elements of the sugar in producing new compounds, but are decomposed separately; while the elements of the sugar, plus a small proportion of the elements of water, form two compounds, alcohol and carbonic acid: $C_{12}H_{22}O_{11} + H_2O = 2(C_2H_5, O + H_2O) + 4CO_2$. Grape sugar, $C_{12}H_{22}O_{11}$, loses 2 eq. of water during fermentation, yielding other-

wise exactly the same results as cane sugar. Sugar of milk, $C_{12}H_{22}O_{11}$, is converted by fermentation into alcohol and carbonic acid, without losing or gaining weight. $C_{12}H_{22}O_{11} = 2(C_2H_5O) + 4CO_2$.

1. OXIDE OF ETHYLE. $AeO = C_2H_4O$.

SYN. Ether. Sulphuric Ether.—This compound is obtained from alcohol, its hydrate, by heating it gently along with sulphuric or phosphoric acid, which removes the water, or at all events causes the separation of the ether from the water. The best process is as follows: 5 parts of alcohol, of at least 90 per cent., are mixed with 9 of sulphuric acid, and the mixture introduced into a retort, where it is rapidly heated to the boiling point, and kept at that point, while by means of a bent tube passing through the cork which stops the tubulure of the retort, and furnished with a stop-cock, fresh alcohol is allowed to enter the retort, so as to keep the liquid constantly at the original level, flowing in exactly as fast as the ether, &c., distils over. The products are condensed in a powerful refrigeratory, such as Liebig's, figured at p. 296: they consist chiefly of ether, with water in such proportion as would convert the ether into alcohol; and a very little alcohol, sometimes none at all. The operation may be advantageously continued until 31 parts of alcohol at 90 per cent. have flowed into the retort, and of course an equal volume of ether and water has distilled over.

This process, as to its final result, may be thus expressed: $AeO, HO + 2(HO, SO_3) = 2(HO, SO_3) + HO + AeO$. That is, the action of heat and oil of vitriol has caused the separation of the ether and the water, which, together, constitute alcohol. And it is to this view of the change, which he considers one of decomposition by contact, that Berzelius applies his theory of a catalytic force. But in reality, the process consists of two stages: the first is the formation of bisulphate of oxide of ethyle (sulphovinic acid), $AeO, HO, 2SO_3$; and the second is the decomposition of this by heat, into AeO and $HO, 2SO_3$. The bisulphate is formed when a mixture of 2 eq. oil of vitriol, 1 eq. alcohol, and from 1 to 3 eq. water, is heated to about 285° ; and at almost precisely the same temperature, the bisulphate is decomposed, especially if the liquid be kept in steady ebullition. Now, the bisulphate contains anhydrous sulphuric acid, ether, and water, $2SO_3 + AeO + HO$; and when decomposed, the sulphuric acid seizes the water, thus preventing the ether from uniting with it, to reproduce alcohol. The ether, therefore, distils over; but as, when the bisulphate was formed, ether, AeO , displaced water, HO , from half the oil of vitriol, so now, when the bisulphate is decomposed, and while its water is retained by the 2 eq. anhydrous acid, the vapors of ether traverse a liquid containing oil of vitriol diluted, both with the water displaced from the other part of it by

the ether, and with the water of the alcohol (which at 90 per cent. amounts to 2 eq. for one of ether, one combined with the ether, to form the alcohol, the other serving to dilute it.) Now a sulphuric acid, thus far diluted, and heated to a temperature even short of 285° , gives off water, and, therefore, the vapor of ether, in passing through this acid, becomes saturated with the vapor of water, without combining with it, and thus ether and water distil over together. At the surface of the boiling, or effervescing liquid, however, the ether produced by the decomposition of the bisulphate is brought into contact with water in the nascent state, also derived from that decomposition, and in this manner, according to Liebig, a little alcohol is reproduced, and distils over with the ether, the ether being produced in the body of the liquid, the alcohol only at the surface. It is certain that a little alcohol generally accompanies the ether, even in the most successful operation; but it is not easy to see how, according to the above explanation, the sulphuric acid which, in the body of the liquid, is able to prevent the ether from combining with water, should fail to do so at the surface. The ether and water, it would appear, are equally in the nascent state in both situations. While, therefore, we admit Liebig's very beautiful explanation of the facts connected with the production of ether, we cannot feel the same certainty in regard to his explanation of the simultaneous occurrence of alcohol. It will now be seen how little necessity there is for resorting to the mysterious agency of catalysis; for the change is not one due to contact alone, but, on the contrary, one depending on strong affinities very nicely balanced, and influenced to a very great extent by the degree of heat employed. The idea that the contact of the oil of vitriol caused the ether and water of alcohol to separate, arose from the circumstance that the formation of the bisulphate of ethyle takes place at a temperature quite close to that at which it is decomposed, and that the formation of the bisulphate in this process had been overlooked.

The crude ether is mixed with an alcoholic solution of potash so as to render it alkaline, and distilled in the vapor-bath, as long as the Sp. G. of the product does not exceed 0.725 at 80° . The ether is then digested for a few days with chloride of calcium, or quick-lime, and rectified once more with one of these substances. When pure, oxide of ethyle is a colorless, very mobile, highly refracting liquid, of Sp. G. 0.725 at 60° . It is very volatile, boiling at 76° , and producing intense cold by its evaporation. It has a pungent, cooling, aromatic taste; and a penetrating, agreeable odor. It is very combustible, and its vapor is apt to form dangerous explosive mixtures with air. When oxidized slowly, it yields aldehyde, aldehydic acid, acetic and formic acids.

Ether is used in medicine as a diffusible stimulant, and in chemistry, as a solvent, especially of organic matters, such as fats fat

oils, essential oils, resins, some acids, and some bases. Its vapor, when mixed with air and inhaled, produces a species of coma, or at least, in most cases, insensibility to pain; and this method is now resorted to to facilitate the performance of severe surgical operations. Great care must be taken to avoid the approach of a light to the mouth of the patient inhaling it, which might cause explosion of the gaseous mixture, or inflammation of the ether, and thus inflict a fatal injury. Care must also be taken to have air enough mixed with the vapor of ether, which, if inhaled alone, would cause asphyxia.

In its relation to other bodies it exhibits the characters of a base, neutralizing acids, and forming compounds which are subject to the laws of double decomposition, like salts of inorganic bases. These salts of oxide of ethyle are, commonly, ethereal liquids, many of them crystallizing at low temperatures, and a good many being solid and crystalline at ordinary temperatures. They are often called ethers with the name of the acid; as, acetic ether, benzoic ether, &c. Those ethers which contain organic acids are, for the most part, fragrant, and it is probable that many fruits owe their fragrance to the presence of the ethers of organic acids. The melon and pine-apple, as well as the apple, have exactly the odor of some such ethers. The formula for the salts of oxide of ethyle corresponds to that for the salts of potash, &c. Thus, as $K O$, \bar{A} represents acetate, and $K O$, \bar{B} benzoate of potash, so $Ae O$, \bar{A} or $Ae O$, $Ac O$, and $Ae O$, \bar{B} or $Ae O$, $Bz O$, represent the acetate and benzoate of oxide of ethyle.

The analogy between ether and metallic protoxides is farther shown in the action of both on hydrochloric acid and its congeners; for while $K O$, with $H Cl$ yield $H O$ and $K Cl$; so $Ae O + H Cl = H O + Ae Cl$; that is, ether, with hydrochloric acid, yields water and chloride of ethyle. The same is true of the bromide, iodide, &c., and by proper means, both the cyanide of ethyle, $Ae Cy$, and the sulphide of ethyle, $Ae S$, may be obtained. In short, we cannot better connect and classify the numerous facts now known in regard to ether, than by adopting the view, which considers it as the basic oxide of ethyle, a compound radical very analogous to a metal.

2. *Hydrate of Oxide of Ethyle*, $Ae O$, $H O = C, H, O, H O$. *Syn. Alcohol*.—This compound is formed when ether and water meet in the nascent state, as we shall see occurs when some of the acid salts of ethyle are heated or otherwise decomposed. But practically, it is produced entirely from sugar, by fermentation. The juice of the grape, or any other saccharine juice, or an infusion of malt, when exposed to the air for a short time, and then to a temperature of from 40° to 85° , soon enters into fermentation and a large quantity of carbonic acid is given off, while the sugar totally disappears and alcohol is found in its place. A pure solution

of sugar in water does not ferment, but on the addition of yeast it does so. The juice of the grape and the infusion of malt both contain, besides sugar, some body which plays the part of yeast, or ferment. This is, in the grape juice, fibrine, and in the malt, gluten, both of which readily enter into putrefaction, when exposed to air and moisture, and being in this state, their particles in motion, this motion is communicated to the particles of sugar, and the existing equilibrium of affinities being thereby disturbed, new compounds are formed, in this case alcohol and carbonic acid.

The subject of fermentation will be afterward fully discussed: in the meantime, it is to be observed that any similar substance, in a state of putrefaction, will induce the fermentation of sugar; as, for example, putrefying flesh, blood, milk, cheese, white of an egg, urine, &c., &c., and that none of these ferments contribute to the production of the alcohol or carbonic acid, but yield ammonia and other products. Crystallized cane sugar, $C_{12}H_{22}O_{11}$, requires the elements of 1 eq. of water, to yield 2 eq. alcohol, C_2H_5O , and 4 eq. carbonic acid $4C_2O_2 = C_4O_4$; and grape sugar, $C_{12}H_{22}O_{14}$, produces, besides the alcohol and carbonic acid, 2 eq. of water. Thus we have $C_{12}H_{22}O_{11} + H_2O = 2(C_2H_5O) + 4C_2O_2$; and $C_{12}H_{22}O_{14} = (C_2H_5O) + 4C_2O_2 + 2H_2O$.

From the fermented liquid, which, in the case of the grape juice, is wine, in that of malt, beer, ale, or wort, the alcohol is separated by distillation, and being more volatile than water, it predominates in the first portions distilled. These constitute, when from wine, brandy; when from a fermented infusion of malt, whiskey; and when from fermented solution of molasses, rum. In these forms it still contains 30, 40, or more per cent. of water and a little volatile odoriferous oil. It is again rectified and the first portions distilled are colorless, and go by the name of spirits of wine. After another rectification they are called rectified spirits of wine. They now contain only alcohol with from 10 to 20 per cent. of water, which is removed by digesting the spirit with quick-lime, and distilling; or by rectifying over dried carbonate of potash, or chloride of calcium.

Pure or absolute alcohol is a colorless mobile fluid, of Sp. G. 0.795 at 60°, and boiling at 173°. It has a burning taste, and a pleasant fruity smell. Rectified spirit of wine, that of 90 per cent., is very similar to it, having the Sp. G. 0.825 to 0.836: ordinary spirit of wine, at 70 per cent., has the Sp. G. 0.880. Pure alcohol has never been frozen. It is very combustible, and produces, in burning, a very intense heat. Hence spirit of wine is much used in lamps for chemical purposes. Alcohol has a strong attraction for water, and on this account acts as an antiseptic, preserving animal and vegetable substances from putrefaction. The strength of alcohol is ascertained by its specific gravity; and all chemical

works contain tables of the relation between the density of the spirit and the per centage.

Alcohol is a powerful diffusible stimulant, and has intoxicating properties. It is much used as a solvent, for many, indeed most vegetable acids and bases, for volatile oils, for resins, and for many salts, even inorganic. Most deliquescent salts are soluble in alcohol, as are the caustic alkalies and iodine. Acids act on alcohol, producing the compound ethers. Solutions made with proof spirit (a mixture of equal volumes of rectified spirit of wine and of water, Sp. G. 0.960), are called tinctures.

3. *Chloride of Ethyle*, $\text{Ae Cl} = \text{C}_4 \text{ H}_2$, Cl —Is prepared by saturating alcohol with hydrochloric acid gas, and distilling the mixture in the vapor bath, collecting the product in a well cooled receiver. It is formed as follows: $\text{Ae O} + \text{H O} + \text{H Cl} = \text{Ae Cl} + 2 \text{ H O}$. It is dried by digestion with chloride of calcium. It is a colorless liquid, Sp. G. 0.874, boiling at 52° , of an aromatic odor, slightly alliaceous. When exposed to the combined action of chlorine and the sun's rays, it yields by substitution a whole series of chlorinized ethers, of which series one extremity is ether ($\text{C}_4 \text{ H}_2$) O ; and the other perchloride of carbon ($\text{C}_4 \text{ Cl}_2$) $\text{Cl} = 2 \text{ C}_2 \text{ Cl}_2$. With an alcoholic solution of protosulphide of potassium K S , it gives chloride of potassium and sulphide of ethyle: $\text{Ae Cl} + \text{K S} = \text{Ae S} + \text{K Cl}$. With hydrosulphide of sulphide of potassium, it yields mercaptan, which is alcohol, in which all the oxygen has been replaced by sulphur: $\text{Ae Cl} + \text{K S}, \text{H S} = \text{K Cl} + \text{Ae S}, \text{H S}$; the latter, mercaptan, being analogous to $\text{Ae O}, \text{H O}$.

4. *Bromide of Ethyle*—Formed by distilling bromine with alcohol and phosphorus. These are first formed when the materials are mixed, phosphorous and hydrobromic acids, and the latter when heated with the alcohol, decomposes it, yielding Ae Br , which resembles the chloride.

5. *Iodide of Ethyle*, Ae I —Formed by a similar process, is analogous to the two preceding compounds.

6. *Sulphide of Ethyle*, Ae S —Is prepared, as above stated, from the chloride by sulphide of potassium. It is a colorless liquid, boiling at 167° , of a strong offensive alliaceous smell.

7. *Hydrosulphide of Sulphide of Ethyle or Mercaptan*, $\text{Ae S}, \text{H S} = \text{C}_4 \text{ H}_2 \text{ S}_2$ or $\text{C}_4 \text{ H}_2, \text{S} + \text{H S}$.—This very remarkable compound is formed when a solution of the double sulphate of lime and oxide of ethyle (sulphovinate of lime) of Sp. G. 1.28, is distilled with its own bulk of a solution of potash of the same density, previously saturated with sulphuretted hydrogen, and converted into $\text{K S}, \text{H S}$. The volatile product, after digesting it with a little oxide of mercury and chloride of calcium, to remove sulphuretted hydrogen and water, is mercaptan. Its formation is thus explained: $(\text{Ca O}, \text{S O}_2 + \text{Ae O}, \text{S O}_2) + \text{K S}, \text{H S} = \text{Ca O}, \text{S O}_2 + \text{K O}, \text{S O}_2 + \text{Ae S}, \text{H S}$. Pure mercaptan is a colorless liquid, very

mobile, boiling at 97° , of Sp. G. 0.842. It has a most penetrating and offensive odor of onions, as it were concentrated, which adheres obstinately to the hair or clothes, so that it is most unpleasant to experiment upon. As above mentioned, it is formed from alcohol by substitution of sulphur for oxygen; and as alcohol is the hydrate of oxide of ethyle, $\text{Ae O}, \text{H O}$, mercaptan is the hydrosulphide of the sulphide of ethyle, $\text{Ae S}, \text{H S}$. The sulphide of ethyle, Ae S , corresponds to the oxide, ether, Ae O .

Mercaptan acts strongly on some metallic oxides, especially those of the noble metals, such as mercury, gold, platinum, &c. The metal takes the place of the hydrogen of the sulphuretted hydrogen in mercaptan; thus $\text{M O} + (\text{Ae S}, \text{H S}) = \text{H O} + (\text{Ae S}, \text{M S})$. The red oxide of mercury is acted on by mercaptan, and converted into a white crystalline compound, called the mercaptide of mercury; oxide of gold forms a gelatinous white mercaptide; and oxide of lead yields lemon yellow crystals of mercaptide of lead, $\text{Ae S}, \text{Pb S}$.

Mercaptan may also be viewed as $\text{H} + \text{Ae S}_2$, in which case the above metallic compounds will have the general formula $\text{M} + \text{Ae S}_2$. Here the supposed radical, the mercaptan of Zeise, is bisulphide of ethyle; so that on either view mercaptan is connected with ethyle.

Zeise has described under the name of thialic oil or ether, another very fetid compound, which seems to be Ae S_3 , or persulphide of ethyle.

Selenide and cyanide of ethyle are both volatile alliaceous offensive liquids, formed when sulphide of ethyle and potash is distilled with selenide or cyanide of potassium. Sulphocyanide of potassium, alcohol, and sulphuric acid, when dissolved together, yield a most offensive volatile liquid, supposed to be, or at all events to contain, sulphocyanide of ethyle. It will be observed that all these compounds of sulphur with ethyle and similar bodies are characterized by odors resembling that of garlic, but so intense and penetrating as to be insupportable. This character is observed in all volatile organic compounds of sulphur, whether artificial, as the above, or natural, as oils of garlic, assafoetida, horseradish, &c.

7. SALTS OF OXIDE OF ETHYLE.

Oxide of ethyle forms both neutral and acid salts. The neutral salts are not at ordinary temperatures decomposed by other salts, like inorganic saline compounds. Thus an alcoholic solution of chloride of calcium does not cause any precipitate in an alcohol solution of oxalate of oxide of ethyle or oxalic ether. But they are easily decomposed by contact with hydrated alkalies, the acid uniting with the alkali, while the oxide of ethyle separates as hydrate, that is, as alcohol. Thus oxalic ether, $\text{C}_2 \text{O}_2, \text{Ae O}$,

with hydrate of potash, K O , H O , yields oxalate of potash K O , C_2O_4 , and hydrate of oxide of ethyle, Ae O , H O .

Oxide of ethyle has a very great tendency to form double salts, in which there are 2 eq. of the acid, 1 eq. of a base, and 1 eq. oxide of ethyle. In these salts, the acid, as in the neutral salts, cannot be detected by the usual tests; and indeed they may be viewed as simple salts, containing a compound acid, of which oxide of ethyle is a constituent, united to the inorganic base. Thus the double sulphate of ethyle and potash, K O , S O_4 , + Ae O , S O_4 , may be viewed as sulphovinate of potash, K O + Ae O , 2S O_4 ; and sulphovinic acid is, on this view, when separated, H O + Ae O , 2S O_4 .

The acid salts of ethyle are on one view double salts, as, for example, the double sulphate formed of sulphate of ethyle, Ae O , S O_4 , with sulphate of water, H O , S O_4 . On the other view, they are compound or coupled acids, and the above example becomes, as mentioned in the last paragraph, sulphovinic acid, H O + (Ae O , 2S O_4), the hydrate of a compound of anhydrous sulphuric acid with ether. These acid salts are decomposed, by boiling with water, into alcohol which distils over, and hydrated acids which remain behind. When distilled with the salts of volatile acids, they yield the ethers of those acids: formiate and acetate of ethyle may be thus obtained. When an acid salt of ethyle is heated with acids not volatile, it often happens that the ethers of these acids are obtained: this is the case with the fatty acids and with some others.

8. *Acid Sulphate of Oxide of Ethyle*, H O , S O_4 , + Ae S O_4 ,—Is also called sulphovinic acid, H O + Ae O , 2S O_4). Sulphuric acid forms no neutral compound with oxide of ethyle. The acid salts is formed when the vapor of ether is conducted into oil of vitriol, or when oil of vitriol is mixed with alcohol and heated to a certain point. To obtain it pure, the double sulphate of ethyle and baryta (sulphovinate of baryta) in solution, is decomposed by sulphuric acid, and the filtered liquid is a solution in water of the acid sulphate. It has a very sour taste, and cannot be concentrated by evaporation, whether at the ordinary temperature or with the aid of heat, without being decomposed into alcohol and sulphuric acid. It forms, with most bases, crystallizable double salts, which are all soluble, so that, for example, the addition of baryta causes no precipitate if the acid be pure. As the acid sulphate itself is called sulphovinic acid, so these double salts are called sulphovinates. It is because all these salts are soluble, that the usual tests cannot detect the sulphuric acid they contain. When, however, their solutions are boiled with a little hydrochloric acid, alcohol is given off, and then the sulphuric acid may be detected as usual. All these salts are decomposed by heat, yielding, according to the temperature, double sulphate of

ethyle and etherole, alcohol, sulphurous acid, olefiant gas, and a sulphate as residue, mixed with charcoal. When heated with hydrated alkalies, they yield sulphates and alcohol. The double sulphate of ethyle and potash crystallizes in shining scales, which are the anhydrous salt, $K O, S O_3 + Ae O, S O_3$. The baryta salt contains 2 eq. of water of crystallization, and forms beautiful tabular crystals, as do also the salt of lime, and the salt of lead, both of which likewise contain 2 eq. of water. These three salts are all composed according to the formula, $M O, S O_3 + Ae O, S O_3 + 2$ eq. water.

9. *Acid Phosphate of Oxide of Ethyle*—Or phosphovinic acid, $P_2 O_5 \left\{ \begin{array}{l} Ae O \\ 2 H O \end{array} \right.$ is formed in the same way as sulphovinic acid, and obtained pure from the double salt of baryta, $P_2 O_5 \left\{ \begin{array}{l} Ae O \\ 2 Ba O \end{array} \right. + 12 H O$. It is a tolerably permanent acid, decomposed only by a high temperature. With bases it forms double salts, in which the 2 eq. water of the acid are replaced by 2 eq. of a protoxide. The baryta salt, the formula of which is given above, crystallizes in pearly scales.

OXIDE OF ETHYLE WITH NITRIC ACID.

10. NITRATE OF OXIDE OF ETHYLE. $Ae O, N O_3$.

When 2 fluid ounces of alcohol, and 1 fluid ounce of pure nitric acid, of Sp. G. 1.4, are distilled together, with the addition of 10 or 20 grains of urea, to destroy any nitrous or hyponitrous acid, the distillation proceeds calmly and smoothly, and the distilled liquor contains water, alcohol, and nitrate of ethyle, which partly separates toward the end of the process, as a heavy oily stratum, and is more completely separated by the addition of water. It is a colorless liquid, of Sp. G. 1.112; which boils at 185° , and is inflammable, burning with a bright white flame. It is quite insoluble in water but very soluble in alcohol; and it possesses a pleasant smell and sweet taste. An alcoholic solution of potash converts it into alcohol and pure nitrate of potash.

11. HYPONITRITE OF OXIDE OF ETHYLE. $Ae O, N O_2$.

Syn. Nitrous Ether. Nitric Ether.—This is best prepared in a state of purity, when a current of hyponitrous acid vapors, derived from starch and nitric acid, is passed through weak alcohol, the product being condensed in Liebig's refrigeratory. The ether is washed with water, and dried by means of chloride of calcium. The whole apparatus must be kept cold, otherwise the action is too violent, and the results very complex. When nitrous ether is made by the usual processes, in which ordinary nitric acid is mixed with alcohol, the product always contains a large proportion of aldehyde, and, in fact, very little of the true ether. The action

in this case is as follows: $2 (C_4 H_6 O_2) + N O_2 = C_4 H_5 O, H O$ (aldehyde), $+ 3 H O + (C_4 H_5 O + N O_2)$. The pure hyponitrous ether, prepared by Liebig's process given above, is a pale yellow liquid, boiling at 62° , of Sp. G. 0.947. It has a very agreeable odor of rennet-apples. With an alcoholic solution of potash, it yields alcohol, and pure hyponitrite of potash. The sweet spirit of nitre or spiritus ætheris nitrosi of the pharmacopœia, is a solution of the impure hyponitrous ether in alcohol.

12. CARBONATE OF OXIDE OF ETHYLE. $Ae O, C O_2$.

SYN. Carbonic Ether.—When oxalic ether is acted on by potassium, there are formed several products, one of which is this ether. When pure, it is an aromatic liquid, of Sp. G. 0.975, boiling at 260° . An alcoholic solution of potash converts it into alcohol and carbonate of potash. Chlorine acts on it, forming products to be described when we treat of the action of chlorine on ethers generally.

13. Double Carbonate of Ethyle and Potash, $K O, C O_2 + Ae O, O O_2$.—Is formed when dry carbonic acid gas is passed through an alcoholic solution of fused potash. A saline mass is obtained, from which, after washing with ether, alcohol dissolves the double salt, leaving carbonate and bicarbonate of potash. The double salt forms pearly scales, which are decomposed by water, into alcohol and bicarbonate of potash.

14. Oxalate of Oxide of Ethyle, $Ae O, C_2 O_3$. **SYN. Oxalic Ether.**—This ether is formed by distilling 4 parts of superoxalate of potash, 5 of oil of vitriol and 4 of alcohol at 90 p. c., mixing the product with 4 times its bulk of water, and washing with water the ether which separates, until all free acid is removed. The ether is then rectified. It is a colorless liquid, of Sp. G. 1.093, boiling at 364° . It has an aromatic smell. If pure, it may be kept under water; but if a trace of alcohol or oxalic acid be present, it is soon resolved into oxalic acid and alcohol when in contact with water. Fixed alcalies cause the same change. When an excess of ammonia is added to it, oxamide is formed: where the ether is in excess, there is formed a substance in beautiful pearly tables, formerly called oxamethane, but now proved to be oxamate of ethyle. These two reactions are easily explained. In the first case, $Ae O, C_2 O_3 + N H_3 = (Ae O, H O) + (C_2 O_3, N H_3)$. In the second, half the ether undergoes the above change, and the other half combines with the oxamide formed: $Ae O, C_2 O_3 + C_2 O_3, N H_3 = Ae O, C_4 N H_5 O_3$. Chlorine acts on oxalic ether, giving rise to products which will be hereafter described along with the results of the action of chlorine on other ethers.

When to an alcoholic solution of oxalic ether there is added enough of an alcoholic solution of potash or soda to decompose the half of the ether, double salts are obtained, of the formula

$M O, C_2 O_3 + Ae O, C_2 O_3$. When the alcoholic solution of the double oxalate of ethyle and potash is treated by fluosilicic acid there is obtained the acid oxalate of ethyle, $H O, C_2 O_3 + Ae O, C_2 O_3$, which is often called oxalovinic acid. The salt of potash, $K O, C_2 O_3 + (Ae O, C_2 O_3)$ (oxalovinic of potash) forms crystalline scales, soluble in alcohol. The oxalovinate of baryta is extremely soluble, and may be used to furnish the other oxalovinates, by acting with it on the soluble sulphates of different bases.

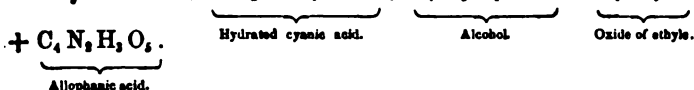
15. *Oxamate of Oxide of Ethyle*, $C_2 N H_3 O = Ae O, C_4 N H_3 O_2 = Ae O, C_2 O_3 + Ad, C_2 O_3$ —Is formed, as above stated, when ammonia is cautiously added to an alcoholic solution of oxalic ether, until a white powder (oxamide) begins to appear. The liquid now yields fine pearly tabular crystals, formerly called oxamethane. It now appears to be oxamate of ethyle, but may also be viewed as oxalate of ethyle, plus oxamide. By an excess of ammonia, it is converted into alcohol and oxamide. The action of ammonia on oxalic ether has been explained above.

16. *Sulphocarbonate of Ethyle and Water*, $Ae O, H O, 2 C S_2$.—When bisulphide of carbon is added to a strong alcoholic solution of potash, a salt is obtained, in colorless or yellow needles, which is a double sulphocarbonate of ethyle and potash, $K O, C S_2 + Ae O, C S_2$. When this salt is acted on by diluted sulphuric or hydrochloric acid, there is obtained a heavy oily liquid. This is the acid compound in question, $H O, C S_2 + Ae O, C S_2$, formerly called xanthic acid, from the yellow color of its salts. With bases it gives rise to double salts, like that of potash, just mentioned, which were called xanthates. The salt of protoxide (suboxide) of copper is lemon yellow.

17. *Allophanate of Oxide of Ethyle*.—This compound is formed when the vapor of hydrated cyanic acid is brought in contact with a mixture of ether and alcohol. It forms brilliant prisms, which may be purified from cyamelide by being dissolved in boiling alcohol, or in boiling water. Its formula is $C_4 N_2 H_4 O_6 = C_4 H_4 O_1 C_4 N_2 H_4 O_6$. It was formerly supposed to consist of 2 eq. hydrated cyanuric acid, 3 eq. oxide of ethyle, and 3 eq. of water; and it is, in fact, resolved by heat into alcohol and cyanuric acid. But Liebig and Wöhler have shown that it is composed of oxide of ethyle and of a new acid, namely, anhydrous allophanic acid, $C_4 N_2 H_4 O_6$. The former view was quite anomalous, since oxide of ethyle unites only with anhydrous acids; and the latter, therefore, brings the compound into the ordinary category of compound ethers.

Allophanic acid is unknown in the hydrated or separate state, the formula of which would be $C_4 N_2 H_4 O_6, H O = C_4 N_2 H_4 O_6$. It forms crystallizable salts with baryta, potash and soda; but when we attempt to isolate it, it is resolved into urea and carbonic acid: $C_4 N_2 H_4 O_6 = C_2 N_2 H_4 O_2 + 2 C O_2$. Allophanic

acid is produced by the action of 2 eq. of hydrated cyanic acid on 1 eq. of alcohol. The water of the alcohol, added to the cyanic acid, produces the new acid, which combines with the oxide of ethyle. Thus, $2 \text{C}_2 \text{N O, H O} + \text{C}_4 \text{H}_6 \text{O, H O} = \text{C}_4 \text{H}_6 \text{O}$



18. *Benzoate of Oxide of Ethyle, or Benzoic Ether*, Ac O, Bz O , —Is best formed by distilling 4 parts of alcohol, 2 of benzoic acid, and 1 of strong hydrochloric acid. The ether distils over with alcohol, from which water separates it. When pure, it is an oily, colorless liquid, of a faint agreeable aromatic odor, and an acrid, spicy taste. Its Sp. G. is 1.054, and it boils at about 410° . Chlorine decomposes it, giving rise to several products, probably by substitution.

19. *Hippurate of Oxide of Ethyle, or Hippuric Ether*, $\text{C}_4 \text{H}_6 \text{O} + \text{C}_{10} \text{N H}_2 \text{O}_2$, —Is formed by passing a current of hydrochloric acid gas through a solution of hippuric acid in alcohol, and heating the mixture for some time near to its boiling point. The addition of water separates a thick heavy oil, which when purified from alcohol and hydrochloric acid, and placed in vacuo, along with sulphuric acid, forms a solid crystalline mass, composed of silky needles. It is decomposed, like other ethers, by alkalies, and by boiling with water.

20. *Salicylate of Oxide of Ethyle*, $\text{C}_4 \text{H}_6 \text{O} + \text{C}_{14} \text{H}_8 \text{O}_2$, —Is obtained by distilling 2 parts of alcohol, $1\frac{1}{2}$ of salicylic acid, and 1 of sulphuric acid. When purified from alcohol, acid, and water, it is a colorless oily fluid, having a sweet smell like that of the corresponding compound of methyle, which occurs naturally in the oil of gaultheria procumbens. It is heavier than water, and boils at 437° . Like the oil of gaultheria, it plays the part of an acid, forming with bases crystallized soluble salts. When exposed to a high temperature with caustic baryta, it yields carbonic acid, and an oil analogous to that obtained from the methyle compound, probably $\text{C}_{18} \text{H}_{16} \text{O}_2$. When fuming nitric acid is added, drop by drop, to the salicylic ether, it dissolves it with a deep red color; water now separates an oil, which soon concretes into a solid mass, which, when dissolved in hot alcohol, yields, on cooling, yellow silky needles. These are indigotate or anilate of oxide of ethyle, $\text{C}_4 \text{H}_6 \text{O} + \text{C}_{14} \text{N H}_4 \text{O}_2$. By the farther action of nitric acid, carbazotic or nitropicric acid is obtained. The indigotic ether dissolves in potash and soda, apparently like the salicylic ether, playing the part of an acid. Indigotic ether does not dissolve in ammonia; left in contact within close vessels, it finally disappears, alcohol is reproduced, and there is formed a new product, anilamide, $\text{C}_{14} \text{N}_2 \text{H}_4 \text{O}_2$, which, when pure, forms brilliant yellow

crystals. When boiled with potash, anilamide yields anilates (indigotate) of potash, and gives off ammonia; for $C_{14}H_9NO_3 + 2H_2O = NH_3 + C_{14}H_8NO_2 + H_2O$. Bromine acts on salicylic ether, producing two compounds; monobromuretted salicylic ether, $C_{14}H_9BrO_3 = C_6H_5O + C_{14}H_8O_3$; and bibromuretted salicylic ether, $C_{14}H_9Br_2O_3 = C_6H_5O + C_{14}H_8O_3$.

The former crystallizes in fine needles, the latter in large pearly scales, which, when melted, form, on cooling, a most beautiful crystallization, formed of large and perfect cubes, like those of bismuth.

COMPOUNDS OF ETHYLE OF UNCERTAIN CONSTITUTION.

1. *Chloro-carbonic Ether*, $C_2H_2ClO_4 = C_2H_2O + C_2\begin{Bmatrix} O_2 \\ Cl \end{Bmatrix}$

—Formed when absolute alcohol is placed in contact with chloro-carbonic acid gas. It appears as an oily liquid, of Sp. G. 1.133, boiling at 200° . It is formed as follows: 2 eq. of chlorocarbonic acid and 1 of alcohol, losing 1 eq. hydrochloric acid, yield 1 eq. of the new ether: $C_2O_2Cl_2 + C_2H_5O_2 = HCl + C_2H_2O_4$. It may be viewed as a compound of oxide of ethyle, with a peculiar acid, $C_2\begin{Bmatrix} O_2 \\ Cl \end{Bmatrix}$; or as carbonic ether, C_2H_2O , plus 1 eq. chlorocarbonic acid, $C\begin{Bmatrix} O \\ Cl \end{Bmatrix}$.

2. *Urethane*. SYN. *Carbamate of Oxide of Ethyle*. *Carbamic Ether*, $C_2H_2NO_4$.—Is formed by the action of ammonia on the preceding compound, along with sal ammoniac, from which it is separated by being sublimed, or rather distilled, when it passes over at a gentle heat, as a liquid which crystallizes on cooling. It is very soluble in water and alcohol, and yields very large crystals. It may be viewed as chlorocarbonic ether, in which amide, NH_2 , has been substituted for the chlorine: $C_2H_2O + C_2\begin{Bmatrix} O_2 \\ N H_2 \end{Bmatrix}$. It is formed as follows: $C_2H_2ClO_4 + 2NH_3 = (NH_3, HCl) + C_2H_2NO_4$.

Berzelius, with much probability, considers it as a compound of oxide of ethyle with an acid, not yet known in the separate form containing the elements of carbonic acid and carbamide, just as oxamic acid does those of oxalic acid and oxamide. On this view its rational formula will be $C_2H_2O + C_2O_2, C_2ONH_2 = C_2NH_2O_4$.

Carbamic acid.

Oxide of ethyle.

It is remarkable that two other compounds, quite distinct in properties have the same empirical formula as urethane or carbamic ether. These are, lactamide, or anhydrous lactate of ammonia,

$C_6 H_4 O_4 + N H_3$; and sarcosine, $C_6 N H_7 O_4$, a new base, derived from kreatine. (See Artificial Alcaloids.)

METAMORPHOSES OF THE COMPOUNDS OF ETHYLE.

When ether or alcohol is passed in vapor through a red-hot tube, it yields aldehyde, water, olefiant gas, and marsh gas: $3 (C_4 H_2 O) = C_4 H_4 O_2 + H O + 3 C_2 H_2 + C_2 H_4$; or $2 (C_4 H_2 O) = C_4 H_4 O_2 + C_2 H_2 + C_2 H_4$. By the action of chloride of zinc on alcohol, there are formed water, and two liquid carbon-hydrogens, $C_4 H_6$ and $C_4 H_8$, together $C_{10} H_{18}$, that is, olefiant gas, or an isomeric modification of it. Now ether and alcohol both contain the elements of water and of olefiant gas; for alcohol is $C_4 H_2 O_2 = 2 H O + C_2 H_4$; and ether is $C_4 H_4 O = H O + C_2 H_4$.

In the manufacture of ether there occur two liquids, one of which is called oil of wine, which is $C_{16} H_{18}$, or very nearly the proportions of olefiant gas, according to the only analysis we have. The other is called the sweet or heavy oil of wine, and is a compound of sulphuric acid with ether, and a body having the same composition in 100 parts as olefiant gas. Sweet oil of wine is $2 S_2 O + Ae O + C_4 H_4$; and as this body, $C_4 H_4$, is called etherole, the compound is named the double sulphate of oxide of ethyle and of etherole. This latter is produced, along with sulphovinic acid, from the reaction of 4 eq. dry sulphuric acid and 3 eq. ether: $4 S O_3 + 3 Ae O = (2 S O_3, Ae O, H O) + (2 S O_3, Ae O, C_4 H_4)$. The same compound is formed when sulphovinate of lime is heated, but is accompanied by alcohol, sulphurous acid, olefiant gas, and a residue of sulphate of lime and charcoal: $2 (Ca O, Ae O, 2 S O_3) = (2 S O_3, Ae O, C_4 H_4) + H O + 2 (Ca O, S O_3)$; and again, $2 (Ca O, Ae O, 2 S O_3) = 2 (Ca O, S O_3) + 2 S O_3 + C_4 H_4 O_2 + C_2 H_2 + C_2 + 2 H O$.

The sweet oil of wine is an oily liquid, quite neutral. It boils at 538° , and has the Sp. G. 1.133. When heated with water it gives off etherole as an insoluble oil, while the liquid contains pure sulphovinic acid. When the etherole, thus separated, is exposed to cold, it deposits crystals of etherine, a compound isomeric with etherole and with olefiant gas.

ETHIONIC, ISETHIONIC, METHIONIC, AND ALTHIONIC ACIDS.

These acids are formed by the action of sulphuric acid on ether and alcohol under various circumstances. When anhydrous acid, $S O_3$, acts on alcohol, or when olefiant gas is absorbed by that dry acid, there is formed a compound, $2 S O_3 + C_4 H_4$, in crystals, which, when put into cold water, produce ethionic acid, $2 S O_3, C_4 H_4 O$. When this solution is heated, 2 eq. of sulphuric acid and 1 of alcohol separate from one half, and there is formed from the other half isethionic acid, $2 S O_3, C_4 H_4 O$, or rather $S_2 O_6$.

$C_4H_4O_2$. Ethionate of baryta, formed by adding baryta to the acid before boiling, is $2SO_3, C_4H_4O, BaO$. From it all the other ethionates may be made. The salts of isethionic acid, like those of ethionic acid, have the same composition in 100 parts as the sulphovينات; but as they contain hyposulphuric acid, their formula is $S_2O_3, C_4H_4O_2 + MO$. They crystallize with remarkable facility. When, in acting on ether with anhydrous sulphuric acid, the mixture gets too hot, there is formed a new acid, methionic acid, the baryta salt of which is $S_2C_4H_4O_2, BaO$, or $S_2O_3, C_4H_4O_2 + BaO$. This acid apparently bears the same relation to oxide of methyle, C_4H_4O , as isethionic does to ether, C_4H_4O . When oil of vitriol in great excess is heated with alcohol, olefiant gas is given off, and the residue is found to contain an acid, the salts of which have the very same composition as the sulphovينات, but differ in crystalline form. This acid is called althionic acid. It is highly probable that the althionates are mixtures or compounds of sulphovينات with isethionates, just as the salts of ethionic acid appear to contain sulphovينات and isethionates or compounds isomeric with these. The two compounds which seem to be distinct and independent are sulphovinic acid, $(AeO, HO, 2SO_3)$, and isethionic acid, isomeric with it, but probably arranged as (HO, AeO_2, S_2O_3) ; the salts of the former being strictly double sulphates of ethyle and bases $(MO, SO_3 + AeO, SO_3)$; and those of the latter being $MO + (AeO_2, S_2O_3)$. Whatever explanation may be given of the fact, it is a fact, that the ethionic and althionic acids and their salts have the same empirical composition as these two acids and their salts, at least according to the best analyses we have.

PRODUCTS OF THE OXIDATION OF ETHYLE AND ITS DERIVATIVES.

The oxidation of alcohol and of ether may be effected in a great variety of ways, and the products are rather numerous, varying according to the amount of oxygen taken up. Thus we have, first aldehyde, then acetic acid, formic acid, oxalic acid, and finally carbonic acid and water. The first effect of oxidation is to destroy the radical ethyle, giving rise to a new and less complex radical acetylene $= C_2H_2$. Afterward we obtain compounds of the still less complex radical, formyle, $= C_2H$, and lastly, compounds of the simple radicals carbon and hydrogen.

We shall here consider, first, the radical acetylene and its compounds: bearing in mind that, while derived from the basic radical ethyle, acetylene has no basic characters whatever, but is, on the contrary, a most distinctly acidifiable radical.

XVII. ACETYLENE. $C_2H_2 + Ac$.

Acetylene is unknown in a separate form, but is easily obtained in the form of hydrated protoxide, or aldehyde, and hydrated peroxide, or acetic acid.

1, HYDRATED OXIDE OF ACETYLE, OR ALDEHYDE. $(C_4 H_3) O, H O.$
 $= Ac O, H O.$

Aldehyde is formed when ether or alcohol is passed through a red-hot tube, or when ether or alcohol are oxidized by nitric acid, or by chlorine, &c. In these cases it is not pure; but it may be obtained quite pure by distilling 2 parts of the compound of aldehyde and ammonia dissolved in 2 parts of water, along with a mixture of 3 parts of oil of vitriol and 4 of water, and rectifying at a temperature of about 80° , over chloride of calcium.

It is a clear, colorless liquid, of a peculiar and powerful ethereal odor, of Sp. G. 0.79 at 65° , and boiling at 70° . It mixes in all proportions with water, alcohol, and ether, and is neutral and inflammable. In contact with the atmosphere it rapidly absorbs oxygen, passing into hydrated acetic acid: for $C_4 H_3, O + H O,$ with O_2 , at once produce $C_4 H_3, O_2 + H O$; or $Ac O, H O + O_2 = Ac O_2, H O$. Aldehyde is a constant ingredient of the nitrous ether of the pharmacopœias.

When heated with caustic potash, it is rapidly converted into the brown matter called resin of aldehyde.* If gently heated with oxide of silver and water, part of the oxide is reduced without effervescence, coating the glass tube with a bright surface of silver, while the water is found to contain a salt of silver, the acid of which contains less oxygen than acetic acid: this is aldehydic or lampic acid, $C_4 H_3 O_2, H O$, or $Ac O_2, H O$. The solution of aldehydate of silver, if filtered and heated to boiling, again deposits metallic silver, while the aldehydic acid becomes acetic. When long kept, even in sealed tubes, aldehyde is transformed

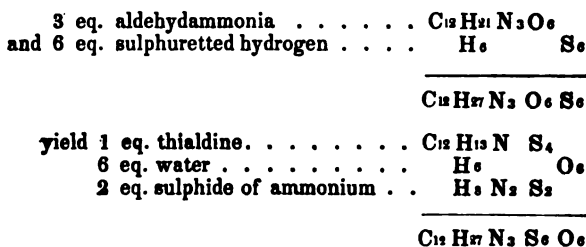
* Potash in acting upon aldehyde, besides producing the above resin, gives rise to an irritating odor, due to a thick yellow oil, smelling like cinnamon. This oil rapidly oxidizes, and is converted into a resin different from that mentioned in the text, containing a considerable quantity of oxygen, while there is formed at the same time acetic and formic acids. Aldehyde with half its bulk of water, and a trace of nitric or sulphuric acid, on cooling to 32° , separates into fine crystals of the metaldehyde of Liebig, and a liquid insoluble in water. This when purified is a new modification of aldehyde; its vapor in density is that of aldehyde, but its properties considerably differ. It is a thin acrid liquid, soluble in alcohol and ether, sparingly in water, boils at 257° , and changes rapidly into a crystalline acid not yet studied. With heat and a trace of sulphuric acid, this modified aldehyde is converted into that of Liebig—thus the same acid forms the substance, and then reconverts it, depending upon a high or low temperature.

Hydrosulphuric acid gas passed through aldehyde and water, deposits a thick oil of an insupportable alliaceous odor, the formula of which is $C_4 H_3 S$ or elaldehyde, the O of which is substituted by S and united to H. Its boiling point is 356° . It is converted to thialdine by absorbing ammoniacal gas. By the action of acids, or by exposure to the air, there is formed acetylic mercaptan, $C_4 H_4 S_2$, which is aldehyde with S_2 instead of O_2 , although this is more probably the sulphurized species of elaldehyde and from it thialdine is immediately derived by $N H_3$ replacing S_2 . With an excess of hydrosulphuric acid, probably both substances may be formed at the same time.

into two isomeric modifications, namely, metaldehyde, a hard crystalline inodorous solid, and elaldehyde, which is liquid.

Aldehydite of Ammonia. SYN. *Aldehydammonia*, $C_4 H_3 O + N H_3 + H O$.—Aldehyde has no basic characters, and rather exhibits a tendency to the acid character, in combining with ammonia, as it does directly to form a crystalline compound. To prepare it, as the substance from which aldehyde is obtained, 6 parts of oil of vitriol, 4 of water, 4 of alcohol, and 6 of peroxide of manganese, in fine powder, are distilled together. The crude product is twice rectified over chloride of calcium: it is now aldehyde, containing a little water, alcohol, and acetic and formic ethers; and this liquid, when mixed with ether, and saturated with ammoniacal gas, yields crystals of the new compound which are washed with ether. These crystals become brown on being kept, even in close vessels, and acquire the smell of burnt feathers. They dissolve in water and alcohol, but hardly in ether. Nitrates of silver forms, in the concentrated solution, a precipitate, insoluble in alcohol, which, when heated, is reduced.

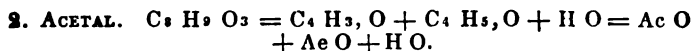
Thialdine.—Liebig and Wöhler have very recently discovered that when an aqueous solution of aldehydammonia is acted on by sulphuretted hydrogen, a little ammonia being previously added, crystals of a new compound are deposited, which has basic properties, and has been called thialdine. It is produced by the action of 3 eq. of aldehydammonia on 6 eq. of sulphuretted hydrogen. Thus,



Thialdine is almost insoluble in water, but very soluble in alcohol and ether. It is deposited, by spontaneous evaporation, from its ethereal solution, in large and beautiful crystals, resembling camphor. It is very volatile and fusible, has an unpleasant aromatic smell and is a powerful base, neutralizing the strongest acids, and forming beautiful crystalline salts. When heated with hydrate of lime, thialdine yields leucoline or quinoline, one of the volatile bases of coal tar.

When aldehydammonia is acted on by seleniuretted hydrogen, an analogous basic compound, selenaldine, is formed; and it appears probable, from the experiments of Liebig and Wöhler, that

telluretted hydrogen is capable also of yielding a similar compound.



Is formed by the action of the oxygen of the air on the vapors of alcohol, under the influence of the black powder of platinum. It is a colorless, very mobile fluid, Sp. G. 0·825, boiling at 203°. It might, according to its composition, be a compound of 3 eq. oxide of ethyle, and 1 eq. acetic acid; for $3 (C_4 H_3 O) + C_4 H_5 O_3 = C_6 H_8 O_3 = (C_6 H_8 O_3)$. But the action of potash which forms resin of aldehyde, and of oil of vitriol which blackens and thickens it as it does aldehyde, indicate pretty certainly the presence of aldehyde; and we, therefore, prefer the formula above given, which makes acetal a compound of aldehyde and oxide of ethyle.

The resin of aldehyde, formed by the action of potash on aldehyde, is little known. Elaldehyde, an isomeric form of aldehyde, which is liquid at ordinary temperatures, but solid at 32°, has a formula exactly triple that of aldehyde, $C_{12} H_{12} O_3$. Met-aldehyde, the other isomeric modification, which, like the preceding, spontaneously forms an aldehyde, when kept, has, no doubt, a similar relation in its formula to that of aldehyde; but its precise formula is not yet known. The density of its vapor would settle the point. It forms very hard prisms, which sublime at 248° without melting. It is worthy of notice that aldehyde, like the corresponding chlorine compound, formed by substitution, chloral, $C_4 Cl_3 O + H O$, undergoes very easily, and even spontaneously, these very singular metamorphoses. This indicates a relation in the constitution of these bodies which cannot be overlooked.



SYN. Aldehydic Acid. Lampic Acid. — It has already been stated that this acid is obtained in combination with oxide of silver, when aldehyde is gently heated with excess of that oxide in water. The solution, when the silver has been separated by sulphuretted hydrogen, contains the acetylous acid, very diluted. It is very easily decomposed, especially by heat, into acetic acid, and a brown resin like that of aldehyde. When the acetylite or aldehydate of silver is decomposed by baryta, so as to precipitate all the oxide of silver, and the acetylite of baryta is now heated with the precipitated oxide of silver, the metal is reduced, and acetate of baryta is now found in the solution. This demonstrates the relation of acetylous to acetic acid: for $Ba O, Ac O_2 + Ag O = Ba O, Ac O_2 + Ag$. This acid is one chief ingredient of the acid produced by the slow combustion of ether in the lamp, with a

spiral of platinum wire on the wick, the platinum continuing red-hot, but no flame appearing, and which acid is called lampic acid.

4. ACETIC ACID. $C_4 H_3 O_3 + H O = Ac O_3, H O.$

Syn. Acetylic Acid. Pyroligneous Acid. Vinegar.—This important acid is formed in two principal ways: first, by the oxidation of alcohol; and secondly, by the destructive distillation of wood. Wine, beer, and other fermented liquors, if exposed to the air, under certain circumstances, undergo what is erroneously termed the acetous fermentation; that is, they attract oxygen from the air; undergo eremacausis of the alcohol they contain, and after a time, contain no alcohol, but in its place, acetic acid; they are, in fact, converted into vinegar. The ultimate change is very simple: $C_4 H_3 O_3 + O_4 = C_4 H_3 O_3, 3 H O, = Ac O_3, H O + 2 aq.$ But we have already seen that there are intermediate steps in the process. The first effect of the oxygen is to remove from the alcohol, or rather from the ethyle in it, 2 eq. hydrogen, thus leaving the radical acetyle, $C_4 H_3$, in the place of the ethyle, $(C_4 H_5) O, H O + O_2 = (C_4 H_3) O, H O + 2 aq.$ In this stage alcohol is simply converted into aldehyde, while 2 eq. water are formed. In the next stage, the hydrated protoxide of acetyle (the aldehyde), or rather the radical $C_4 H_3$, takes up 2 additional equivalents of water, and thereby becomes acetic or acetylic acid: $(C_4 H_3) O, H O + O_2 = (C_4 H_3) O_3, H O.$

Such being the action of the oxygen of the air on alcohol, it is obvious that the process of acetification is no fermentation but a case of eremacausis or slow combustion. But, as was formerly explained, the state of eremacausis is induced by contact of a body in that state, or even in the state of fermentation or putrefaction, and the presence of a ferment is required to commence the process of eremacausis of alcohol. Pure alcohol, exposed to air alone, is not acetified; but if its vapor, mixed with air, comes in contact with platinum powder, eremacausis is induced. Hence, if alcohol be placed in a flat basin under a bell jar, beside a small flat dish, containing platinum black, the bell jar, is, in a few seconds, filled with the pungent smell of aldehyde, and in an hour or two, the acetification is nearly complete. Here the platinum, by virtue of its singular power of causing gases or vapors to unite on its surface, acts as a ferment, or, as it may be called, an excitant, inducing the slow combustion, and acting as a carrier of oxygen from the air to the alcohol.

In wine or beer, there is present an actual ferment in the shape of gluten or fibrin, at least in all cases where the vinous fermentation has not decomposed the whole of the ferment. In these cases, exposure to the air for a short time causes the decomposition of the gluten, &c., to recommence, and this state of decomposition,

consisting in part, no doubt, of *eremacausis*, being mechanically communicated in the shape of motion to the particles of alcohol, slow combustion commences and continues till every trace of alcohol has been acetified, when the process is arrested for want of fuel, that is, of alcohol. Where, in the fermentation of wine, (as sherry), or of beer, (as Bavarian beer), all ferment has been destroyed or removed, these liquors do not become sour when exposed to air, and if we wish to acetify them, we must add yeast or some other ferment. So, also, when we wish to make strong vinegar by the acetification of brandy or of whiskey, we have to add a ferment, such as yeast, and expose the mixture to a certain temperature, in open vats. By carefully attending to all these principles, the process of acetification may be very much abridged. The following is the rapid process now followed on the Continent. There is made a mixture of 1 part of alcohol at 80 p. c., 4 to 6 parts of water and $\frac{1}{10}$ of a ferment, such as vinegar, honey, or must of beer. A large, high barrel is packed with twigs or shavings of beech, previously soaked in strong vinegar, and holes are drilled in the middle and upper part of the barrel to admit a free circulation of air. The mixture is now warmed to from 75° to 80°, and made to trickle slowly upon the shavings and through the barrel, thus exposing an immense surface to the air. The temperature rises rapidly to 95° or 105°, and if a proper supply of air be given, continues at that point during the operation. When the mixture has been three or four times passed through the barrel, it is found perfectly acetified: this may take place in from 24 to 36 hours. Should the supply of fresh air, that is, of oxygen, be deficient, much aldehyde is produced, which, from its volatility, is carried off as vapor and lost. This was long a source of great loss to the makers, and the cause could not be traced, until Liebig, by the discovery of aldehyde, explained it, and showed how to avoid the loss, by giving a due supply of air. The manufacturer now obtains, as nearly as can be expected, the theoretical quantity of vinegar from his spirits. Any aromatic substance, or essential oil, or even a trace of wood vinegar (contaminated with creosote, &c.) will arrest the progress of acetification.

The peculiar pleasant smell of good vinegar, in addition to that of pure diluted acetic acid, is owing to the presence of acetic ether. Distilled vinegar is a tolerably pure, but weak acetic acid; but to obtain acetic acid pure and strong, we must have recourse to the salts of acetic acid, which, when distilled with moderately strong sulphuric acid, yield pure acetic acid, mixed with more or less water.

The pyroligneous acid is contaminated with pyroxylic spirit and with oil of tar. When combined with soda, lime, or oxide of lead, these salts may be easily purified by crystallization, and by heating them so far as to expel or destroy the oily impurities.

The pure salts, distilled with sulphuric acid, yield acetic acid, identical with that from true vinegar.

Hydrated Acetic Acid, Radical Vinegar, or Crystallizable Acetic Acid, $\text{AcO}_2, \text{H}_2\text{O}$.—Is obtained by distilling 3 parts of dry powdered acetate of soda with 9.7 of oil of vitriol, as pure and concentrated as possible: $\frac{1}{8}$ of the acid distils over by the heat spontaneously developed in the mixture; a gentle heat expels the rest. The product is rectified and exposed to a cold of 23° or 24° , when crystals of the hydrate are formed in a weaker liquid. The crystals are allowed to drain, and then melted, and again exposed to cold. The crystals of this second operation are generally free from all superfluous water. At temperatures below 60° hydrated acetic acid is solid; at 62° or 63° it melts, forming a liquid which sometimes continues liquid at a much lower temperature, and then crystallizes from some very trifling cause. The Sp. G. of the liquid is 1.063; it boils at 248° ; has a pungent, peculiar, but agreeable smell, and a burning acid taste. It raises a blister on the skin, and soon produces a painful sore, like a mineral acid. It is miscible in all proportions with water, alcohol, and ether. It dissolves camphor and essential oils; and the aromatic vinegar is a solution in it of camphor, with a little oil of lemons and bergamot, &c. Strong acetic acid, in this form, is used as a diffusible stimulant, applied to the nostril in faintness or sickness. It may be used, also, externally as a very powerful rubefacient and epispastic. The hydrated acid is combustible. It is decomposed by anhydrous sulphuric acid, yielding a new acid, sulphacetic acid: also by chlorine, yielding, by substitution, chloracetic acid. The vapor of acetic acid, passed through a red hot tube, yields carbonic acid and acetone, $\text{C}_2\text{H}_2\text{O}$: the same transformation occurs when acetic acid is heated with bases.

The salts of acetic acid are, almost without exception, soluble in water: the acetates of silver and protoxide of mercury are sparingly soluble. The formula for the neutral acetates is MO , $\text{C}_4\text{H}_3\text{O}_5$, or M , $\text{C}_4\text{H}_2\text{O}_4$. There are hardly any acid salts; but a considerable number of basic salts, as basic acetates of lead and copper.

Acetate of Oxide of Ethyle, or Acetic Ether, AeO , AcO_2 .—Is easily prepared by distilling 10 parts of acetate of soda, 16 of oil of vitriol, and 6 of alcohol. The product is rectified over lime and chloride of calcium. It may also be obtained by distilling any sulphovinate with strong acetic acid. In either case, acetic acid is brought in contact with nascent ether, and combines with it. Acetic ether is a colorless liquid, of a refreshing odor, very combustible. It boils at 165° ; its Sp. G. is 0.89. It is easily decomposed by alkalies, yielding an acetate and alcohol. Acids also decompose it. It is always present, in small quantity, in wine vinegar, which owes its flavor to this compound.

Acetate of Ammonia.—There is a well-known febrifuge and diaphoretic remedy called the spirit of mindererus, which is a diluted solution of acetate of ammonia, formed by neutralizing distilled wine vinegar with carbonate of ammonia. A more uniform preparation, although stronger than that usually employed here, is made by neutralizing 6 parts of aqua ammoniæ, Sp. G. 0.96, with strong acetic acid, and adding enough water to make up twenty-four parts. This, being uniform, can easily be reduced if desirable. There is an acid acetate of ammonia, which forms deliquescent needles. Acetate of potash, K O , Ac O_3 , is obtained as a fibrous crystalline mass, very deliquescent, which has a warm saline taste. It is much used as a diuretic. When heated with arsenious acid, it yields oxide of cacodyle; a substance of most remarkable composition and characters, $\text{C}_4 \text{H}_6 \text{As}_2 \text{O}$. Acetate of soda, Na O , $\text{Ac O}_3 + 6 \text{ aq.}$, is formed from pyroligneous acid, and is the form in which the acid is brought in order to be purified from oil of tar. The salt is melted at a moderate heat, and roasted, then redissolved, filtered through charcoal, evaporated, again melted, and so on, until it becomes snow-white. 10 parts of the crystals of salt, after the first fusion, while still slightly colored, being distilled with 6 of oil of vitriol, yield what is called wood vinegar, sufficiently pure for use, but requiring 7 waters to reduce it to the average strength of wine vinegar. Acetates of baryta, strontia, and lime, all crystallize readily. The first is used as a test; the last in the manufacture of acetic acid and all other acetates from pyroligneous acid. Acetate of alumina, $\text{Al}_2 \text{O}_3$, 3 Ac O_3 , prepared by mixing solutions of alum and acetate of lead (or of baryta) is very soluble. It is much used in the above form, containing sulphate of potash, as a most valuable mordant in dyeing and calico printing. When heated it deposits an insoluble basic salt, which adheres tenaciously to the cloth, and afterward combines firmly with the coloring matter. The pure acetate of alumina, formed from sulphate of alumina and acetate of baryta, is not so decomposed by heat, but requires the presence of a neutral salt. Acetate of manganese, Mn O , Ac O_3 , formed by acting on sulphate of manganese by acetate of lime, is much used in calico printing, as it gives, with bleaching liquor, a rich bronze brown. Acetate of zinc, Zn O , Ac O_3 , $+ 3 \text{ aq.}$, is used in medicine and pharmacy. Acetate of protoxide of iron, Fe O , Ac O_3 , is used as a mordant. Acetate of peroxide of iron, $\text{Fe}_2 \text{O}_3$, 3 Ac O_3 , is formed by precipitating acetate of lead with persulphate of iron. It has the same valuable properties as acetate of alumina, depositing a basic salt, when heated with neutral salts, and is much prized as a mordant. Acetate of lead; *a.* neutral, Syn. Sugar of lead; is best prepared by dissolving litharge in acetic acid, and crystallizing. It has a sweet astringent taste, and is much used as an astringent and styptic in diarrhœa, dysentery, and various hemorrhages.

It is poisonous, especially where it forms carbonate: it ought therefore never to be given without abundance of vinegar being taken by the patient. The crystals are $\text{Pb O}, \text{Ac O}_3 + 3 \text{ aq.}$ *b.* Sesquibasic, $3 \text{ Pb O} + 2 \text{ Ac O}_3$, soluble pearly scales. *c.* Tribasic or subacetate of lead is formed in crystals by mixing 1 vol. of aqua ammoniæ with 5 of a cold saturated solution of the neutral salt, and setting it aside. It forms long needles. The solution, or Goulard's extract, is made by digesting 7 parts of litharge with 6 of sugar of lead and 30 of water, till the oxide, which is not dissolved, has become white. It is much used as a lotion, and to precipitate gum, organic acids, albumen, caseine, extractive matter, &c., from organic mixtures, and solutions. Its formula is $3 \text{ Pb O} + \text{Ac O}_3$. *d.* Sexbasic, formed by adding the last or any of the previous acetates of lead to an excess of ammonia. It forms a crystalline powder, very sparingly soluble, which is $6 \text{ Pb O} + \text{Ac O}_3$. It usually exists in white lead, along with carbonate of lead.

Acetate of Copper, a. neutral — Appears in two forms: as dark green oblique rhombic prisms, becoming opaque in air, $\text{Cu O}, \text{Ac O}_3 + \text{aq.}$; and as dark blue transparent crystals of great beauty, $\text{Cu O}, \text{Ac O}_3 + 5 \text{ aq.}$ These latter, heated to 86° , lose 4 eq. of water, and fall to a powder of the green salt. *b.* Bibasic or verdigris, $2 \text{ Cu O} + \text{Ac O}_3 + 6 \text{ aq.} = \text{Cu O}, \text{Ac O}_3, 5 \text{ aq.} + \text{Cu O}, \text{H O}$. Verdigris is prepared by a tedious process, and is seldom pure, containing usually different basic acetates. *c.* Sesquibasic, $3 \text{ Cu O}, 2 \text{ Ac O}_3 + 6 \text{ aq.}$ *d.* Tribasic, $6 \text{ Cu O}, 2 \text{ Ac O}_3 + 3 \text{ aq.}$ The two last occur in the verdigris of commerce. All these salts are poisonous.

Schweinfurt or Vienna Green — Is a double salt, formed of acetate and arsenite of copper, $\text{Cu O}, \text{Ac O}_3 + 3 (\text{As}_2 \text{ O}_3, \text{Cu O})$; is formed when 10 parts of verdigris, suspended in water, are left to digest for 24 hours, after mixing them with a hot solution of 8 parts of arsenious acid in 100 of water. A dirty green precipitate first appears, which, on standing, changes to a most beautiful green, much used as a paint.

Acetate of Protoxide of Mercury — Is obtained in sparingly soluble silvery scales, by adding acetate of potash to protonitrate of mercury, both hot. It blackens when exposed to light. It is used in medicine, especially on the Continent.

Acetate of Silver, $\text{Ag O}, \text{Ac O}_3$ — Very much resembles the preceding salt. It is occasionally used as a test. It is very sparingly soluble.

ACTION OF CHLORINE, BROMINE, ETC., ON ETHYLE, ACETYLE, AND THEIR DERIVATIVES.

1. OXIDE OF ETHYLE AND CHLORINE.

When dry chlorine is made to act on ether, with the aid of the sun's rays, there are produced several compounds. The first is a

heavy oily liquid, oxychloride of acetylene $C_2 H_2 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$; which is dry acetic acid, with 2 eq. of oxygen replaced by 2 eq. of chlorine. With water, it forms acetic and hydrochloric acids. When the action is pursued, there is obtained a compound $C_2 Cl_2 O$, which is ether, in which all the hydrogen is replaced by chlorine. The first compound may be connected with this one by being viewed as ether in which hydrogen is partially replaced by chlorine, $C_2 \left\{ \begin{smallmatrix} H_2 \\ Cl_2 \end{smallmatrix} \right. O$. Finally there is obtained a crystallizable solid compound, $C_2 Cl_4$, which may be represented as $C_2 Cl_2, Cl_2$, showing that the oxygen of ether is also here replaced by chlorine. This last body is chloride of carbon, $C_2 Cl_4$ for $C_2 Cl_4 = 2 C_2 Cl_2$. Besides these compounds, there are others formed at the same time, more difficult to separate, and which are doubtless the intermediate links of the chain of substitutions, beginning with ether $C_2 H_2 O$, and ending with chloride of carbon, $C_2 Cl_4, Cl_2$. The other members of the series which are more easily obtained by the action of chlorine on chloride of ethyle (see below, p. —), are, $C_2 H_2, Cl_2$, chloride of ethyle: $C_2 \left\{ \begin{smallmatrix} H_2 \\ Cl_2 \end{smallmatrix} \right. Cl : C_2 \left\{ \begin{smallmatrix} H_2 \\ Cl_2 \end{smallmatrix} \right. Cl : C_2 \left\{ \begin{smallmatrix} H_2 \\ Cl_2 \end{smallmatrix} \right. Cl : C_2 \left\{ \begin{smallmatrix} H \\ Cl_2 \end{smallmatrix} \right. Cl$; and as the compound, $C_2 Cl_2 O$ is formed, it is probable that there is another series beginning with ether, and ending with $C_2 Cl_2 O$, in which the oxygen remains unchanged. The above are not all cases of substitution with preservation of the type; for the compound $C_2 \left\{ \begin{smallmatrix} H_2 \\ Cl_2 \end{smallmatrix} \right. O$, may very likely be $C_2 H_2 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$, belonging to the type of acetic acid, rather than that of ether. These compounds are as yet but little known: it is obvious that the simultaneous occurrence of so many similar compounds must render the study of them exceedingly complicated and difficult.

The body $C_2 H_2 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$, or oxychloride of acetylene, when acted on by sulphuretted hydrogen, yields two new compounds, in which its chlorine is partially or entirely replaced by sulphur. Both are crystalline; one, the oxysulphide of acetylene, $C_2 H_2 \left\{ \begin{smallmatrix} O \\ S_2 \end{smallmatrix} \right.$ forms large colorless prisms: the other, oxychlorosulphide of acetylene, $C_2 H_2 \left\{ \begin{smallmatrix} O \\ Cl \end{smallmatrix} \right.$ forms yellow tabular crystals.

2. SALTS OF OXIDE OF ETHYLE WITH CHLORINE.

When chlorine acts on these salts, or ethers, their oxide of ethyle is acted on as if separate, but in many cases the acids remain combined with the new chlorinized compounds; or the

acids also are acted on, and the products derived from them combined with those derived from the ether.

Acetic ether yields a compound $C_2 H_5 Cl_2 O_4$, which may be viewed as $C_4 H_3 \begin{Bmatrix} O \\ Cl_2 \end{Bmatrix} + C_4 H_3 O_2$, that is, acetate of the oxychloride of acetylene. When the compound is further exposed to the action of chlorine at a high temperature, it yields a series of compounds, in which its hydrogen is gradually replaced by chlorine, till the compound $C_2 Cl_5 O_4$ is left, which is called perchloruretted acetic ether. Acetic ether is $C_2 H_5 O_4$; and we have the acetate of oxychloride of acetylene, $C_2 \begin{Bmatrix} H_5 \\ Cl_2 \end{Bmatrix} O_4$; then

$C_2 \begin{Bmatrix} H_4 \\ Cl_2 \end{Bmatrix} O_4$; $C_2 \begin{Bmatrix} H_3 \\ Cl_4 \end{Bmatrix} O_4$; $C_2 \begin{Bmatrix} H_2 \\ Cl_6 \end{Bmatrix} O_4$; $C_2 \begin{Bmatrix} H \\ Cl_8 \end{Bmatrix} O_4$; and $C_2 Cl_5 O_4$. The two last can be obtained, with certainty, pure: the others, after $C_2 \begin{Bmatrix} H_5 \\ Cl_2 \end{Bmatrix} O_4$, are so mixed that it is very difficult to obtain them pure enough for analysis.

When benzoic ether, $Ae O$, $Bz O$, is acted on by chlorine, it loses 2 eq. hydrogen, and 1 eq. oxygen, and takes up 3 eq. chlorine, producing a compound which may be viewed as containing chloride of benzoyle and oxychloride of acetylene, $Bz Cl + C_4 H_3 \begin{Bmatrix} O \\ Cl_2 \end{Bmatrix} = C_{10} H_3 Cl_3 O_3$.

Oxalic ether, exposed to the action of chlorine, under the influence of the direct rays of the sun, loses all its hydrogen, which is replaced by chlorine. $(C_4 H_5) O$, $C_2 O_3$ thus becomes $(C_4 Cl_5) O$, $C_2 O_3$. The latter is called chloroxalic ether. It is a crystallizable solid, fusible at 288° . Dry ammonia acts on it as on oxalic ether, producing chloroxamethane, a crystalline compound analogous to oxamethane. It was formerly stated that oxamethane, $C_8 H_7 N O_6$, has the composition of oxamate of oxide of ethyle $(C_4 H_5) O + C_4 H_2 N O_5$; or of oxalic ether plus oxamide $(C_4 H_5) O$, $C_2 O_3 + N H_2$, $C_2 O_2$. In like manner, chloroxamethane represents chloroxalic ether plus oxamide: $(C_4 Cl_5) O$, $C_2 O_3 + N H_2$, $C_2 O_2 = C_8 H_2 Cl_5 N O_6$. When chloroxamethane is left in contact with ammonia, it takes up 2 eq. of water, and forms a new salt, chloroxalovinate of ammonia, $C_4 Cl_5 O$, $N H_4 O$, $2 C_2 O_3$, which is very deliquescent. From the corresponding salt of soda the chloroxalovinic acid may be obtained, which may of course be viewed as an acid oxalate of the compound $C_4 Cl_5 O$. Its formula is, $C_4 Cl_5 O$, $C_2 O_3 + H O$, $C_2 O_3$.

By the action of alcohol on chloroxalic ether, there is formed a neutral oil, $C_8 Cl_5 O_7$, which contains the elements of anhydrous chloroxalovinic acid, $C_4 Cl_5 O$, $2 C_2 O_3$; and when dissolved in potash, yields chloroxalovinate of potash.

Carbonic ether, by the action of chlorine, yields two products :

1st, bichloruretted carbonic ether, $C_4 \begin{Bmatrix} H_2 \\ Cl_2 \end{Bmatrix} O, C O_2 = C_2 H_2 Cl_2 O_2$; and 2d, perchloruretted carbonic ether, $C_4 Cl_2 O, C O_2 + C_2 Cl_2 O_2$. The former is an oily liquid; the latter crystallizable.

Chloride of ethyle, $(C_2 H_5) Cl$, when acted on by chlorine, yields a very remarkable series of products, in which the hydrogen is gradually replaced by chlorine, as mentioned at p. 263, to which I refer for the formulæ. I shall only mention that the compound there represented as $C_4 \begin{Bmatrix} H_4 \\ Cl \end{Bmatrix} Cl, = C_4 H_4 Cl_2$, corresponds to aldehyde, and is, therefore, probably $(C_2 H_5) Cl + H Cl$, just as aldehyde is $(C_2 H_5) O + H O$. In like manner, the compound $C_4 \begin{Bmatrix} H_2 \\ Cl_2 \end{Bmatrix} Cl = C_4 H_2 Cl_3$, corresponds to dry acetic acid, $C_2 H_3 O_2$. The action of potash on these two compounds confirms this view, according to which the former is hydrochlorate of protochloride, and the latter perchloride of acetylene.

When alcohol, the hydrated oxide of ethyle, is subjected to the long-continued action of chlorine, aided by the sun's rays, there is formed, after a very tedious operation, a remarkable compound called chloral, the empirical formula of which is $C_2 H Cl_2 O_2 = C_2 Cl_2 O + H O$. This compound represents aldehyde or hydrated oxide of acetylene, in which the hydrogen of the acetylene has been replaced by chlorine. It is an oily liquid, boiling at 199° , of Sp. G. 1.502. Like aldehyde, chloral, when kept, is spontaneously converted into an insoluble solid compound, which has the same composition as chloral itself. In contact with water, chloral is soon converted into a solid hydrate, which dissolves in a larger quantity of water. It contains 1 eq. chloral and 2 eq. water. When heated with caustic alkalies, chloral produces formiate of the alkali and perchloride of formyle, $C_2 H Cl_2 O_2 + H O, K O = (C_2 H) O_2, K O + (C_2 H) Cl_2$. The perchloride of formyle, in contact with the alkali, is partly decomposed, yielding chloride of the metal.

According to Städeler, chloral is formed when starch is heated with hydrochloric acid and peroxide of manganese.

Pure acetic acid when acted on by chlorine and the sun's rays, is converted into a crystallizable acid, the chloracetic acid, $C_2 Cl_2 O_2, H O$. As acetic acid may be considered to be aldehyde plus 2 eq. oxygen, or hydrated peroxide of acetylene, so chloracetic acid is chloral plus 2 eq. oxygen, or hydrated peroxide of $C_2 Cl_2$, which may be called chloracetylene. Chloracetic acid forms tabular crystals, fusible at 113° , boiling at 390° . The density of the liquefied acid at 113° is 1.617. When heated with excess of potash, it yields first carbonic acid and perchloride of formyle, $C_2 Cl_2 O_2, H O +$

$2\text{KO} = 2(\text{KO}, \text{CO}_2) + \text{C}_2\text{HCl}_2$. The perchloride of formyle is partly converted by another portion of potash, into formiate of potash and chloride of potassium: $\text{C}_2\text{HCl}_2 + 4\text{KO} = 3\text{KCl} + \text{KO}, \text{C}_2\text{HO}_2$.

With bases, chloracetic acid forms salts which are very analogous to the acetates; and it is very important here to observe, that both in chloral and chloracetic acid, the substitution of chlorine for all the hydrogen of the radical (acetylo) of aldehyde and acetic acid, has not affected the general chemical characters of the compounds; that, in other words, the original type has been retained. We have also seen, in the preceding pages, among the products of the action of chlorine on oxide of ethyle and on the salts of oxide of ethyle, that oxide of ethyle, $\text{C}_4\text{H}_2\text{O}$, is converted into oxide of chlorethyle, $\text{C}_4\text{Cl}_2\text{O}$, without the type being altered: the oxide of chlorethyle forming with the acids previously combined with oxide of ethyle, compounds perfectly analogous to the ethers from which they are obtained.

The sulphide of ethyle is readily acted on by chlorine, and yields a yellow oily liquid, of Sp. G. 1.673, boiling at 320° , of a most fetid odor, the formula of which is $\text{C}_4\text{H}\left\{\begin{smallmatrix} \text{H} \\ \text{Cl}_4 \end{smallmatrix}\right.\text{S}$. Here 4 eq. of hydrogen of the compound, $\text{C}_4\text{H}_2\text{S}$, are replaced by chlorine.

Heavy muriatic ether is an oily liquid, formed by the action of moist chlorine on alcohol. It is obviously a mixture, and probably contains aldehyde, chloride of ethyle, chloral, and products intermediate between aldehyde and chloral.

Bromal, $\text{C}_4\text{Br}_2\text{O}, \text{HO}$.—This compound, analogous to chloral, is formed by the action of bromine on alcohol. It forms a hydrate with 3 eq. water. By caustic alcalies it is resolved into formic acid, which combines with the alkali, and perbromide of formyle.

Iodine does not, so far as is known, produce a compound corresponding to chloral and bromal; but a solution of iodine in alcohol, treated with an alcoholic solution of potash, yields formiate of potash and peroxide of formyle, C_2HI_2 .

By the action of chlorine on alcohol, holding in solution hydrocyanic acid on a metallic cyanide, there is produced a crystalline compound, the empirical formula of which appears to be $\text{C}_6\text{H}_4\text{N}_2\text{Cl}_2\text{O}_2$. This is equal to 3 eq. aldehyde, 2 eq. chloride of cyanogen, and 2 eq. water; but the true nature of this compound is unknown.

3. COMPOUNDS DERIVED FROM ALCOHOL, BUT OF UNCERTAIN CONSTITUTION.

Olefiant Gas. SYN. *Hyduret of Acetylo*, $\text{C}_4\text{H}_4 = \text{C}_4\text{H}_2, \text{Cl}$ = AcH .—This well-known compound is generally present in coal gas, oil gas, and, in general, in all gaseous mixtures produced by the action of heat on organic substances. It is best obtained

pure by heating 1 part of alcohol with 6 or 7 of oil of vitriol. There is produced some ether, then sweet oil of wine, and lastly, a mixture of sulphurous acid and olefiant gases. By passing the gas through milk of lime, the sulphurous acid is removed, and by then passing it through oil of vitriol, the ether, alcohol, and water which may be present, are likewise separated. Pure olefiant gas has been already described (see p. 140, Part I): here we shall attend to its combinations. It is absorbed by anhydrous sulphuric acid, forming the crystalline compound formerly mentioned, $2 \text{S O}_2 + \text{C}_4 \text{H}_4$, which, in contact with water, produces ethionic acid. When mixed with its own volume of chlorine, both gases are condensed into a liquid, the composition of which is $\text{C}_4 \text{H}_4 \text{Cl}_2$. This is the oily compound, from which the gas was called olefiant gas: the oil is often called the oil of the Dutch chemists, having been discovered by an association of chemists in Holland.

When mixed with 2 vol. of chlorine, and set fire to, the whole of the carbon of the gas is deposited in the solid form or as smoke, while all the hydrogen forms hydrochloric acid, $\text{C}_4 \text{H}_4 + \text{Cl}_4 = 4 \text{HCl} + \text{C}_4$.

The oil of olefiant gas, or of the Dutch chemists, $\text{C}_4 \text{H}_4 \text{Cl}_2$, may be viewed as composed of hydrochloric acid, and a chloride of acetylene: $\text{HCl} + \text{C}_4 \text{H}_2 \text{Cl}$. When acted on by an alcoholic solution of potash, chloride of potassium and water are formed, and a new compound separates, which is the protochloride of acetylene, $\text{C}_4 \text{H}_2 \text{Cl}$. It is gaseous at ordinary temperatures, has an alliaceous smell, and burns, like all similar chlorinized compounds, with a dark-red flame, edged with green. At 0° it condenses into a liquid.

When this protochloride of acetylene is acted on by perchloride of antimony, it yields, among other products, a liquid, boiling at 240° which is, $\text{C}_4 \text{H}_2 \text{Cl}_2$, and therefore has the same composition as perchloride of acetylene, formerly mentioned. But the action of potash dissolved in alcohol, proves that these two compounds are distinct, and that the one now under consideration is, $\text{C}_4 \text{H}_2 \text{Cl}_2 + \text{HCl}$. At all events, it yields chloride of potassium, water, and a very volatile liquid, $\text{C}_4 \text{H}_2 \text{Cl}_2 = 2 (\text{C}_2 \text{H, Cl})$, or, in other words, protochloride of formyle.

By continuing the action of chlorine, there is obtained a compound, $\text{C}_4 \text{H}_2 \text{Cl}_4 = \text{C}_4 \text{HCl}_3 + \text{HCl}$; which, with potash, yields the body, $\text{C}_4 \text{HCl}_3$; and the final result of this action is the protochloride of carbon, $\text{C}_4 \text{Cl}_4 = 4 \text{CCl}$; which, however, unites with chlorine to produce the sesquichloride, $\text{C}_4 \text{Cl}_4 + \text{Cl}_2 = \text{C}_4 \text{Cl}_6 = 2 \text{C}_2 \text{Cl}_3$.

The perchloride of acetylene has been already mentioned as a product of the action of chlorine on ether: it is $\text{C}_4 \text{H}_2 \text{Cl}_2 = \text{Ac Cl}_2$.

The oil of olefiant gas, $\text{C}_4 \text{H}_4 \text{Cl}_2$, which may be considered the hydrochlorate of chloride of acetylene, $\text{C}_4 \text{H}_2 \text{Cl} + \text{HCl}$, is best

prepared by passing olefiant gas into perchloride of antimony, as long as it is absorbed. The mixture, if distilled, yields the oil in question. It is purified by alternate distillation with water and sulphuric acid, and finally drying it with chloride of calcium. It is a very mobile liquid, of a pleasant ethereal smell, and a very sweet taste; it boils at 180° , is insoluble in water, soluble in alcohol and ether.

When subjected to the action of chlorine, it yields hydrochloric acid, and products rich in chlorine. Among these are the hydrochlorate of chloride of formyle, $C_2 H Cl + H Cl$, which distills at 240° , and the bichloride of formyle, $C_2 H, Cl_2$, which distills at 275° . This last is finally converted into sesquichloride of carbon, for $C_2 H, Cl_2 = C_2 Cl_2 + H Cl$.

Chlorethral is the name given by D'Arcet to a compound formed by the action of chlorine on olefiant gas, containing both alcohol and ether. Its empirical formula is, $C_4 H_4 Cl O$; so that it may be aldehyde, plus oil of olefiant gas; $C_4 H_3 O, H O + C_4 H_3 Cl, H Cl = 2 (C_4 H_4 Cl O)$; or oxychloride of acetylene, plus oxide of ethylene: $C_4 H_3 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right. + C_4 H_3 O = 2 (C_4 H_4 Cl O)$.

The true nature of this compound is unknown.

Bromine forms with olefiant gas, a liquid compound analogous to the oil of olefiant gas. Its formula is $C_4 H_3, Br + H Br$. Iodine forms, with olefiant gas, a solid compound, which would appear to be $C_4 H_3, I + H I$, rather than $C_4 H_3, I + H I$.

Anhydrous sulphuric acid absorbs olefiant gas, producing a white crystalline solid, $2 S O_3 + C_4 H_4$; which, when dissolved in water, forms, with 1 eq. of water, ethionic acid, $2 S O_3 + C_4 H_3 O = C_4 H_3 O_3 + S_2 O_5$. The original crystalline compound has been called sulphacetylic acid.

4. ACTION OF BICHLORIDE OF PLATINUM ON ALCOHOL.

This action is very complex, yielding aldehyde, chloride of ethylene, chloride of acetylene, and other volatile compounds, along with a salt, composed of chloride of platinum and chloride of acetylene. It is possible that 3 eq. of oxide of ethylene, with 4 eq. of bichloride of platinum, may yield 1 eq. aldehyde, 1 eq. water, 4 eq. hydrochloric acid, and 2 eq. of the new salt: $3 (C_4 H_3 O) + 4 Pt Cl_2 = C H_3 O, H O + H O + 4 H Cl + 2 (C_4 H_3 Cl + Pt_2 Cl)$. Zeise considers the salt to be $C_4 H_4 + 2 Pt Cl$, which formula differs from the preceding in containing 1 eq. hydrogen more. Malaguti supposes it to be $C_4 H_3 O + 2 Pt Cl$; but Zeise has shown that it contains no oxygen. It does not crystallize, but forms a gummy mass, spontaneously decomposing when kept.

When a solution of bichloride of platinum in alcohol is digested with a little hydrochloric acid, and chloride of potassium, the alcohol distilled off, and the residue neutralized by carbonate of

potash, a yellow crystallizable salt is obtained, which contains the preceding compound, plus 1 eq. chloride of potassium, $C_4 H_3 Cl + Pt_2 Cl + K Cl$. Similar double salts are formed with chloride of sodium and chloride of ammonium.

These double salts form with ammonia a yellow precipitate, which is $C_4 H_3 Cl, Pt Cl + N H_3$.

5. ACTION OF HEAT ON ACETIC ACID AND THE ACETATES.

Acetone. SYN. *Pyroacetic Spirit.* *Mesitic Alcohol.* — Formula, $C_3 H_3 O$. Is formed when acetic acid is passed through a tube, heated to low redness, along with carbonic acid, carbonic oxide, and carburetted hydrogen; also, when the acetate of an alkali or alkaline earth is exposed to heat, when a carbonate is left, and acetone distils over. It is best prepared by distilling a mixture of 2 parts of crystallized acetate of lead, and 1 part quick-lime. Its formation is easily explained; for anhydrous acetic acid, $C_4 H_3 O_2$, contains the elements of 1 eq. carbonic acid and 1 eq. acetone. $C_4 H_3 O_2 = CO_2 + C_3 H_3 O$. Acetone is also formed in the distillation of sugar, of citric acid, of tartaric acid, &c. It is purified by rectification, until its boiling point becomes constant, at 100° . It is a clear and colorless liquid, of Sp. G. 0.7921, and has a peculiar smell and a pungent taste. It is miscible with water, alcohol and ether, in all proportions; and is separated from water by the addition of caustic potash, chloride of calcium, or other salts insoluble in acetone.

Heated with hypochlorite of lime, it is converted into carbonic acid and perchloride of formyle. When prepared by the distillation of acetates, acetone is accompanied by an oily liquid, $C_6 H_3 O$.

Acetone contains, in 3 eq., the elements of 1 eq. carbonic ether and 1 eq. olefiant gas, (hyduret of acetylene): $C_4 H_3 O, CO_2 + C_4 H_3, H = C_6 H_3 O_2 = 3(C_3 H_3 O)$; or, in 4 eq., we have the elements of 1 eq. acetic ether, and 1 eq. hyduret of acetylene: $C_4 H_3 O, C_4 H_3 O_2 + C_4 H_3, H = C_8 H_3 O_4 = 4(C_3 H_3 O)$. Kane considers acetone to be $C_6 H_3 O_2 = C_6 H_3 O, HO$; that is, the hydrated oxide of a radical $C_6 H_3$, which he calls mesitylene. In this view, acetone is analogous to alcohol, and $C_6 H_3 O$, the oxide of mesitylene, to ether. But although Kane has obtained this compound, $C_6 H_3 O$, and also another, $C_6 H_3 Cl$, his chloride of mesitylene, and although he has likewise formed double salts containing sulphuric acid and the elements $C_6 H_3 O$, yet the analogy is far from being established. It has not yet been found possible to reproduce acetone, the alcohol, from the supposed ether of the series, as we can reproduce alcohol from the salts of oxide of ethylene. Moreover, in these double salts, the body $C_6 H_3 O$, does not act as a base, but is only coupled with the acid, as naphthalene in sulphonaphthalic acid. We shall not, therefore, enter

into minute details of the theoretical views alluded to. It is sufficient to enumerate the supposed radical mesityle, $C_6 H_3$; its oxide, $C_6 H_3 O$, oxide of mesityle; its hydrated oxide, $C_6 H_3 O, H O$ (acetone); the chloride and iodide of mesityle, $C_6 H_3 Cl$ and $C_6 H_3 I$; the acid sulphate of oxide of mesityle, $C_6 H_3 O, H O, 2 S O_3$ (sulphomesitylic acid); the double salts of this sulphate, the formula of which is, $C_6 H_3 O, H O, 2 M O, 2 S O_3$; and a compound discovered by Zeise, containing oxide of mesityle with chloride of platinum, $C_6 H_3 O, Pt Cl$.

The action of nitric acid on acetone gives rise to a new product, nitrite of oxide of pteyle, $C_6 H_3 O, N O_2$; phosphoric acid appears to form a compound acid with acetone; and when phosphorus, iodine and acetone are distilled together another acid is obtained, which appears to contain hypophosphorous acid.

When chlorine acts on acetone, it produces a liquid, $C_6 H_4 Cl_2 O_2$, which is called mesitic chloral.

Mesitylene, $C_6 H_4$. This compound is obtained when acetone is distilled with fuming sulphuric acid. It is an oily liquid boiling about 300° . Acetone $2 (C_6 H_3 O) = C_6 H_4 + 2 H O$; and this explains its production.

When mesitylene is acted on by nitric acid, it yields a liquid, $C_6 H_4 O_2$, called by Kane, mesitic aldehyde. But when chlorine is passed through mesitylene, a crystalline solid is obtained, containing a new radical pteyle, combined with chlorine, $C_6 H_4 + Cl_2 + C_6 H_3 Cl + H Cl$. The compound $C_6 H_3 Cl$ is the chloride of the supposed new radical pteyle, $C_6 H_3$. Kane has described a compound in yellow scales, which he considers to be iodide of pteyle. It is very desirable that the whole of the compounds derived from acetone should be again carefully examined, since their true constitution cannot be considered as established.

COMPOUNDS CONTAINING ARSENIC, DERIVED FROM ACETYLE.

When acetate of potash is heated along with arsenious acid, a very remarkable liquid is obtained, which is the oxide of a new radical. This liquid, which is spontaneously inflammable, and has a most offensive alliaceous smell, has been long known in an impure state, under the names of liquor of Cadet, and alcarsine. Bunsen, by a long series of the most profound and persevering researches, established its true character, as the oxide of the radical cacodyle. He has even succeeded in obtaining the radical itself in the separate state, and in establishing the most perfect analogy between that radical and a metal, in all its chemical relations.

XVIII. CACODYLE. $C_4 H_6 As = Kd$.

The radical is best obtained from the chloride of cacodyle, $Kd Cl$, by the action of zinc at 212° . Chloride of zinc is formed, and cacodyle is set free. It is rectified in an apparatus filled with

carbonic acid gas, to prevent decomposition. It is a clear liquid, refracting light strongly. When cooled, it crystallizes in large square prisms, and acquires, when pure, the appearance of ice. Its smell is insupportably offensive, and its vapor is highly poisonous. The two latter characters belong to all the compounds of cacodyle, with hardly an exception. Cacodyle is spontaneously inflammable in the air; a rod moistened with it instantly takes fire when exposed to the air. It forms two distinct oxides; the protoxide, $Kd O$ (alkarsine), and cacodylic acid, $Kd O_3$.

Protoxide of Cacodyle. $C_4 H_8 As_2 O = Kd O$.

Syn. Alkarsine.—This is the chief ingredient of the liquor of Cadet; it is purified by repeated rectifications in an atmosphere of carbonic acid, and is, when pure, a limpid ethereal liquid, refracting light powerfully; it boils at about 300° , and at -9° it crystallizes in white scales of a satiny lustre. Its smell is most offensive, and its taste very nauseous. If placed on the skin, it causes violent itching, and if taken internally it is a most energetic poison. It is sparingly soluble in water, more soluble in alcohol and ether. Like cacodyle, it takes fire when exposed to the air. When left under water, it gradually disappears, being for the most part converted into cacodylic acid. The production of oxide of cacodyle is very simple; 2 eq. dry acetic acid and 1 eq. arsenious acid yield 4 eq. carbonic acid and 1 eq. oxide of cacodyle: $2(C_4 H_8 O_3) + As_2 O_3 = 4 CO_2 + C_4 H_8 As_2 O$.

Cacodylic Acid. $Kd O_3 = C_4 H_8 As_2 O_3$.

Syn. Alcargene.—Formed by the gradual oxidation of the protoxide, under water. It forms oblique four-sided prisms, brittle, and of a glassy lustre. They have no smell, and are soluble in water and alcohol. Its salts do not crystallize. Many reducing agents convert it into the protoxide by removing 2 eq. of oxygen. It is not in the least poisonous.

There appears to be an intermediate oxide, $Kd O_2$; but it has not been obtained in a state of purity.

Chloride of cacodyle, $Kd Cl = C_4 H_8 As_2 Cl_4 = Kd Cl$, is obtained by heating a compound of oxide of cacodyle and corrosive sublimate along with hydrochloric acid: $Kd O, Hg Cl_2 + H Cl = Kd Cl + H O + Hg Cl_2$. It is a volatile, horribly fetid liquid, the vapor of which attacks strongly the lining membrane of the nose, and provokes a flow of tears. When exposed to the air, it deposits crystals of an oxychloride of cacodyle, $Kd O + 3 Kd Cl$. The iodide, bromide, and fluoride of cacodyle, are in all points analogous to the chloride; and form, when exposed to the air, oxyiodide, oxybromide, &c.

Sulphur forms with cacodyle three compounds: the protosulphide, $Kd S$, is obtained by distilling chloride of cacodyle with

hydrosulphide of sulphur of barium : $\text{Kd Cl} + \text{Ba S}, \text{H S} = \text{Kd S} + \text{Ba Cl} + \text{H S}$. It is a clear, volatile, very fetid liquid, heavier than water. It dissolves sulphur, forming the bisulphide Kd S_2 , which is a very permanent compound. The persulphide, Kd S_3 , is a sulphur acid, and forms sulphur salts which are very permanent, with the sulphides of highly basic metals. The sulphur salt of cacodyle and lead, $\text{Pb S}, \text{Kd S}_3$, crystallizes beautifully.

Cyanide of cacodyle, $\text{Kd Cy} = \text{C}_4 \text{H}_6 \text{As}, \text{C}_2 \text{N}$, is formed by distilling bichyanide of mercury with water and oxide of cacodyle. When pure it forms large brilliant crystals, very fusible and volatile. The vapor of this compound is so poisonous as to be in the highest degree dangerous to the experimenter.

COMPOUNDS OF CACODYLE CONTAINING PLATINUM.

Chloride of cacoplatyle, $\text{C}_4 \text{H}_7 \text{As Pt O}_2, \text{Cl}$. This compound is formed when an alcoholic solution of bichloride of platinum is added to a similar solution of chloride of cacodyle, when a reddish-brown precipitate is formed, which, being boiled with water, gives a solution from which, on cooling, needles of the new compound are deposited. Bromide of cacoplatyle and iodide of cacoplatyle may be formed from the chloride, and are analogous to it. The former appears in large yellow crystals, the latter in golden micaceous scales.

When the chloride is acted on by sulphate of silver, there is obtained, along with chloride of silver, the sulphate of the oxide of cacoplatyle, $\text{C}_4 \text{H}_7 \text{As Pt O}_3, \text{SO}_3$. It forms white crystalline grains.

The radical of these singular compounds, cacoplatyle, may be represented as composed of protoxide of platinum, water, and cacodyle : $\text{Pt O}, \text{H O}, \text{C}_4 \text{H}_6 \text{As}$. We have therefore the following series, which, like those derived from the bases containing platinum, formerly described, throws much light on the nature of the vegetable bases :

Radical, cacoplatyle,	$\text{Pt O} + \text{Kd} = \text{C}_4 \text{H}_6 \text{As Pt O}$.
Chloride of do., anhydrous,	$\text{Pt O}, \text{Kd} + \text{Cl}$
Chloride, hydrated,	$\text{Pt O}, \text{Kd} + \text{Cl} + \text{H O}$
Chloride, ammoniated,	$\text{Pt O}, \text{Kd} + \text{Cl} + \text{N H}_3$
Oxide, hydrated,	$\text{Pt O}, \text{Kd} + \text{O} + \text{H O}$
Sulphate, hydrated,	$(\text{Pt O}, \text{Kd} + \text{O}, \text{H O}) + \text{S O}_3$.

It is to be particularly borne in mind that this radical, whose basic character is quite obvious, contains two metals, arsenic and platinum, quite foreign in general to organic compounds.

The existence of cacodyle itself, and the perfect analogy which may be traced between it and the simple metals, in their relations to all other substances, render the results of the researches of Bunsen, which have been so very briefly described in this work, of the very highest importance to the theory of organic compounds, and especially to that of compound radicals.

APPENDIX TO ETHYLE AND ACETYLE. — SUGAR.

Sugar, as the substance from which alcohol and all the compounds of ethyle are exclusively obtained, comes properly to be considered here as an appendix to these compounds. There are several kinds of sugar, capable of undergoing fermentation and of producing alcohol. These are, cane sugar; grape sugar; (sugar of starch; of honey; diabetic sugar); sugar of milk; and uncrystallizable sugar. The sugar of mushrooms has been found to be mannite, which is not fermentescible.

1. *Cane Sugar*, $C_{12}H_{22}O_{11} + 2H_2O$ — Occurs in great abundance in the sugar-cane, the beet-root, the maple, besides many other vegetables. It is extracted from the juice of these plants by crystallization, the evaporation being conducted at as low a temperature as possible. It crystallizes with great facility, either in small grains by rapid cooling of a strong syrup, as in loaf sugar; or in large distinct crystals by a slow process, as in sugar candy. The above formula represents the composition of pure crystallized sugar.

Sugar forms large transparent hard crystals, which melt at 302° , or, according to Peligot, at 356° , forming a viscid liquid, which on cooling forms a transparent amorphous mass, barley sugar. This, when kept, gradually becomes crystalline, opaque, and friable. About 420° sugar is converted into a brown tasteless mass, caramel, losing 3 eq. of water.

Sugar dissolves in $\frac{1}{3}$ of its weight of cold, and in any quantity of boiling water; a solution saturated at 230° becomes a solid crystalline mass on cooling (tablet): a solution saturated in the cold is viscid, and is called syrup. Syrup, when long boiled, loses the property of crystallizing. The crystallization of sugar from syrup is also prevented by the addition of $\frac{1}{10}$ of oxalic, citric, or malic acids. When boiled with diluted sulphuric acid, cane sugar is converted into grape sugar. With strong sulphuric acid it produces a dark brown liquid, containing a new acid, sulphosaccharic acid. Nitric acid converts it into saccharic acid, oxalic acid, and carbonic acid.

When boiled with very diluted sulphuric acid, sugar absorbs oxygen from the air, and produces formic acid, and a brown matter identical with ulmine, formed by the decay of wood. Sugar prevents the precipitation of many metallic solutions by alkalies; and when mixed with oxide of copper and potash, the oxide of copper is dissolved, forming a purple solution, which, on boiling, deposits red suboxide of copper. It reduces partially the oxides of many metals, when boiled with their solutions.

Sugar forms crystallizable compounds with the alkalies, oxide of lead, and chloride of sodium. When in contact with the lining membrane of the stomach of a calf, or with the caseine of milk, sugar is transformed into lactic and butyric acids.

Sugar, if taken along with nitrogenized food, may be called nutritious : it would appear, however, to act chiefly in contributing to the support of respiration, and thus keeping up the animal heat. An animal, confined to sugar as food, soon dies from want of nitrogenized or albuminous matter, with the symptoms of starvation.

When a solution of sugar is examined by polarized light, it gives rise to a series of rings of the prismatic colors, when the plane of polarization is made to rotate from left to right.

SUGAR WITH BASES AND SALTS.

With lime, sugar forms a sparingly soluble compound, $C_{12}H_{22}O_{11} + \begin{Bmatrix} CaO \\ HO. \end{Bmatrix}$ With baryta, it forms a crystallizable compound,

$C_{12}H_{22}O_{11} + \begin{Bmatrix} BaO \\ HO. \end{Bmatrix}$ With oxide of lead it yields an insoluble compound, $C_{12}H_{22}O_{11} + 2 PbO$; and with common salt it yields a crystalline compound, $2 C_{12}H_{22}O_{11} + \begin{Bmatrix} 3 HO \\ NaCl. \end{Bmatrix}$

2. *Grape Sugar.* SYN. *Glucose.* *Diabetic Sugar.* *Starch Sugar*, $C_{12}H_{22}O_{11}$. — This sugar occurs in the juice of many fruits, and is besides a product of the metamorphosis of starch, cane sugar, woody fibre, sugar of milk, &c., when boiled with diluted acids. It may also be obtained from starch by the action of infusion of malt, or of diastase. It occurs in the urine of those affected with diabetes mellitus. The crystals which form in honey are likewise grape sugar.

It is best extracted from dried grapes, or honey, and is also prepared on the large scale from starch. 1 part of starch is boiled with 4 of water, and from $\frac{1}{10}$ to $\frac{1}{5}$ of sulphuric acid, during 36 or 40 hours ; or an infusion of malt is added to jelly of starch, which soon becomes liquid, and, in a few hours, is converted into sugar. When acid is used, it is neutralized by chalk, the solution of sugar filtered, and evaporated to a syrup, or, if required, to a dry mass. In this process, starch, $C_{12}H_{20}O_{10}$, takes up 4 eq. water, and produces grape sugar, $C_{12}H_{22}O_{11}$; so that 100 parts of pure starch yield, or ought to yield, 122 of grape sugar. The same explanation, only varying the quantity of water, applies to the conversion into grape sugar of cane sugar, $C_{12}H_{22}O_{11}$; woody fibre, $C_{12}H_{20}O_{10}$; and sugar of milk, $C_{12}H_{22}O_{11}$, these compounds requiring 3, 6, and 2 eq. of water respectively to form grape sugar.

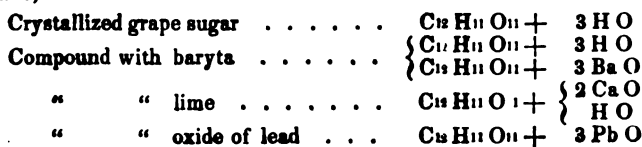
The action of infusion of malt is not explained : all that we know is, that this infusion, or a solution of diastase, a substance contained in it, do actually cause starch to take the form of grape sugar. It is probable that the diastase is in a state of decomposition, and may act as a ferment. The action of the acid would seem to be equally obscure ; but there is some reason to think

that there is first formed, as in the case of ether, a coupled acid, or acid salt, which, like sulphovinic acid, is decomposed by boiling. According to De Saussure, sulphuric acid and starch actually form a crystallizable compound.

Grape sugar crystallizes from alcohol in square tables or cubes : a concentrated syrup of it yields only a mass formed of crystalline grains. It is much less soluble, requiring $1\frac{1}{2}$ parts of cold water, and less sweet to the taste, than cane sugar : in fact, 1 part of cane sugar sweetens as much as $2\frac{1}{2}$ of grape sugar. It is much more soluble in cold alcohol than cane sugar. At 212° grape sugar loses 2 eq. of water ; when heated beyond 284° it becomes caramel. Hot water dissolves any quantity of grape sugar, but the syrup is not nearly so viscid as that of cane sugar. Solution of grape sugar exhibits the prismatic rays with polarized light when the plane of polarization is rotated from right to left, the colors being less brilliant. Now, as cane sugar, when fermented, first becomes grape sugar, the colored rings at first shown by it when the plane of polarization is rotated from left to right disappear during fermentation, but reappear when rotation is made from right to left.

Grape sugar is easily distinguished from cane sugar by the action of acids and bases. Strong sulphuric acid dissolves without charring it, forming sulphosaccharic acid ; and the alcalies or alkaline earths, which do not decompose cane sugar unless very concentrated, rapidly convert grape sugar into a brown matter. Peroxide of lead converts it, at 212° , into basic formiate of lead, carbonate of lead, and water.

With baryta and lime, and oxide of lead, grape sugar forms compounds which it is difficult to obtain pure. That with baryta appears to contain 3 eq. baryta for 2 eq. of sugar, and as the baryta replaces water in such compounds, it is probably $C_{24}H_{32}O_{22}$, $3 Ba O = C_{24}H_{32}O_{22} \begin{cases} 3 Ba O \\ 3 H O. \end{cases}$ The compound with lime appears to be $C_{12}H_{16}O_{12}$, $2 Ca O$; and that with lead $C_{12}H_{16}O_{11}$, $3 Pb O$. If we suppose the dry grape sugar to be $C_{12}H_{16}O_{11}$, and to combine with 3 eq. water and 3 eq. base, then we should have,



But the compound which grape sugar forms with common salt, and which crystallizes very readily, does not agree exactly with this view. The crystals are $2 (C_{12}H_{16}O_{11}) + Na Cl + 2 H O$; and at 212° they lose the two equivalents of water.

The sulphosaccharic acid, above mentioned as being formed when grape sugar is acted on by oil of vitriol, has not been fully examined. It forms a soluble salt with baryta.

With organic acids grape sugar forms compounds, the sugar in which cannot be brought to crystallize. Hence organic acids in vegetable juices act injuriously by first converting cane sugar into grape sugar, and then forming with it uncrystallizable compounds.

When sugar is boiled with hydrochloric acid, it yields different brown products, according to the strength of the acid. With equal parts of acid and water, it yields a body, $C_{24}H_{11}O_8$: with a weaker acid, two brown compounds; a soluble one, $C_{40}H_{14}O_{22}$, and an insoluble one, $C_{60}H_{16}O_{14}$. When boiled with diluted sulphuric acid, two substances are formed, which are nearly black; one, sacchulmine, insoluble, and the other sacchulmic acid, soluble in ammonia. The latter is $C_{35}H_{10}O_{15}$.

When boiled with alcalies, cane sugar is first converted into grape sugar, and then into formic acid, and two new acids, the glucic acid and the melassic acid. Glucic acid is very soluble, and its formula is either $C_{24}H_{16}O_{15}$, $6H_2O$, or $C_{12}H_8O_8$, $3H_2O$. It is chiefly formed before the application of heat, which converts it into melassic acid. This latter acid is formed from sugar by the joint action of heat and alcalies. It has a very dark color, and when separated by hydrochloric acid, appears as a black flocculent deposit. Its formula is $C_{24}H_{12}O_{10}$ (?)

Caramel, the black matter formed by heating sugar to about 400° , has the formula of anhydrous cane sugar, $C_{12}H_{22}O_{11}$. It dissolves readily in water, forming a solution like sepia, which is tasteless when pure. The caramel of commerce contains a good deal of undecomposed sugar.

When sugar is distilled with 3 parts of lime, it yields a liquid which is a mixture of acetone and metacetone. Metacetone is a colorless liquid, of an agreeable odor, boiling at 183° , and insoluble in water. Its formula is C_6H_8O ; and it may be considered as 2 eq. acetone, $C_6H_8O_2$, minus 1 eq. water.

1 eq. of anhydrous sugar	$C_{12}H_{22}O_{11}$
Contains 1 eq. acetone	C_3H_8O
1 eq. metacetone	C_6H_8O
3 eq. carbonic acid	$3C^2O_2$
1 eq. water	H_2O
Together	$C_{15}H_8O_8$

The formation of these products is therefore easily accounted for.

When sugar is heated with hydrate of potash, several products are formed, but among them is an acid, $C_6H_8O_4 = C_6H_8O_3, HO$, which is metacetic acid, evidently derived from metacetone by oxidation at the expense of the hydrate. It is very similar to

acetic acid, and like it, belongs to the series of volatile acids of the general formula, $(C H) n + O_4$.

ACTION OF NITRIC ACID ON SUGAR.

Saccharic Acid, $C_{12} H_{10} O_{11}$, $5 H O$? or $C_6 H_4 O_7$, $H O$ — Is one of the products of the action of diluted nitric acid on cane or grape sugar. When stronger acid is used, oxalic and carbonic acids are the chief products. When sugar has been heated with 2 parts of nitric acid and 10 of water, the acid liquid gives, with basic acetate of lead, an insoluble saccharate of lead, which is decomposed by sulphuretted hydrogen, and the acid solution so far neutralized with potash that on evaporation it yields crystals of the acid saccharate of potash. This salt is purified, again converted into saccharate of lead, and again the lead salt is decomposed by sulphuretted hydrogen. The acid this time is pure. It crystallizes with difficulty.

This acid has been supposed to be quintibasic, and to form five series of salts, but the latest researches of Heintz lead to the conclusion that it is either $C_6 H_4 O_7$, $H O$, or $C_{12} H_8 O_{14}$, $2 H O$. Owing to the very discordant results of different experimenters, we shall not here enter into details which are uncertain. Saccharic acid forms a crystallizable acid salt with potash, and definite salts with many other bases. It is isomeric with mucic acid: for $C_{12} H_8 O_{14}$, $2 H O$ is the probable formula of mucic acid.

The saccharate of silver, when gently heated under water, is decomposed, the silver being reduced; and as this occurs without effervescence, the reduced metal adheres to the glass, and forms a bright mirror surface. The other saccharates are only interesting in respect to their composition. On the whole, saccharic acid is a compound of high theoretical interest, and the formation of two isomeric acids, saccharic and mucic, by the action of nitric acid on cane and grape sugar on the one hand, and on sugar of milk on the other, is a fact which may hereafter lead to a knowledge of the true constitution of the different kinds of sugar.

Notwithstanding the fact that cane sugar is easily converted into grape sugar, and that the formulæ differ only by 3 eq. water, it is evident that these two kinds of sugar differ more than if they were merely different hydrates of the same compound. Strong mineral acids instantly decompose cane sugar, but have little action on grape sugar; while alcalies, which combine with cane sugar to form crystalline compounds, rapidly convert grape sugar into dark compounds, glucic and melassic acids. And although both sugars agree in undergoing the same (vinous) fermentation, yet it is most probable that cane sugar, before fermenting, becomes grape sugar.

When vegetable juices containing cane sugar are evaporated, the presence of organic acids causes its conversion into grape sugar; and when lime is added, to clarify the juice, the action of

the lime on grape sugar when evaporated, produces glucic and melassic acids; in other words, renders much sugar dark and uncrystallizable, converting it into molasses. A great part of the loss owing to this cause has of late years been avoided by carefully neutralizing with sulphuric acid as soon as the lime has effected the clarification.

3. *Sugar of Milk, or Lactine*, $C_{12}H_{22}O_{11} + 5H_2O = C_{12}H_{22}O_{11}$ — Is obtained by evaporating clarified whey till it crystallizes. When pure it forms hard white crystals, soluble in 5 or 6 parts of cold, and $2\frac{1}{2}$ of hot water. The taste of the crystals is feeble, but a concentrated solution tastes very sweet. It is insoluble in ether and alcohol. It stands between cane sugar and grape sugar in composition; for while cane sugar is $C_{12}H_{22}O_{11}$, and grape sugar $C_{12}H_{22}O_{11}$, lactine is $C_{12}H_{22}O_{11} = 2(C_6H_{12}O_6)$. By boiling with diluted acids, it is converted into grape sugar. By the action of nitric acid, it yields mucic or saccholactic acid. It combines with ammonia and with oxide of lead. Its presence prevents the precipitation of many metallic solutions. Sugar of milk is susceptible of the vinous fermentation, and it is well known that some nations prepare an intoxicating liquor from milk by fermentation. There is reason to think that previous to fermentation, it is, like cane sugar, converted into grape sugar; and at all events milk does not ferment until an acid has been formed in it, which acid converts lactine into grape sugar.

Sugar of milk forms two compounds with oxide of lead: first, neutral, $C_{12}H_{22}O_{11}$, 5 Pb O; second, basic, $C_{12}H_{22}O_{11}$, 10 Pb O.

Mucic acid, $C_{12}H_{22}O_{14} + 2H_2O$, is formed when diluted nitric acid acts on sugar of milk, gum, or mannite. It is a white crystalline powder, of a feebly acid taste, soluble in 6 parts of boiling water, which deposits nearly the whole on cooling. Its solution, when long heated and evaporated, yields the modified mucic acid. Mucic acid dissolves in oil of vitriol with a crimson color. When heated it blackens, and yields among other products, pyromucic acid.

Mucic acid is bibasic, and forms two series of salts, one with 2 eq. fixed base, the other with 1 eq. fixed base, and 1 eq. water. These salts have little interest. The mucate of oxide of ethyle or mucic ether, crystallizes in 4 sided prisms, soluble in hot water. When boiled with a base, it yields alcohol, and mucate of the base. Its formula is $C_{12}H_{22}O_{14} + 2AeO$.

Modified mucic acid is more soluble in water, soluble in alcohol, from which solution it is deposited in square tables. Its aqueous solution, saturated at the boiling point, deposits on cooling ordinary mucic acid. Its salts are more soluble than the mucates, but the acid in them easily passes into the ordinary acid. It is probable that the modified acid contains 1 eq. of water more than the other.

Pyromucic acid, $C_{10}H_2O_8 + H_2O$, is formed by the dry distillation of mucic acid. 1 eq. of mucic acid, $C_{12}H_{10}O_{10}$, contains the elements of 1 eq. pyromucic acid, $C_{10}H_4O_8$, 6 eq. water, H_2O , and 2 eq. carbonic acid, C_2O_4 . Pyromucic acid forms brilliant white scales, fusible at 266° , and volatilizes completely at a temperature somewhat higher. It is soluble in water and alcohol. Its salts are not important. Pyromucate of oxide of ethyle, $C_{10}H_2O_8, AeO$, is a solid crystallizable compound, fusible at 93° , volatile at 410° . Chlorine acts on this ether, forming a new compound, $C_{14}H_8Cl_4O_8$, the constitution of which is quite uncertain.

4. *Sugar of Mushrooms.* — Wiggers obtained from ergot of rye a saccharine compound, crystallizing in transparent rhombic prisms, soluble in water and alcohol, and susceptible of the vinous fermentation. An analysis of this sugar gave the formula $C_{12}H_{12}O_{11}$, that is, grape sugar, minus 1 eq. water. This may be a distinct kind of sugar; but the mushroom sugar of Braconnot is mannite or manna sugar.

We have seen that starch and woody fibre may be converted into grape sugar by boiling with dilute sulphuric acid; in like manner, salicine and phloridzine, boiled with the same acid, yield saliretine and phloretine, in each case along with grape sugar. But the action of the infusion of malt is still more singular; we have seen that starch by contact with infusion of malt is rapidly converted into grape sugar. This action is ascribed to the presence of diastase, a nitrogenized body which exists in malt, and which, while it causes the conversion of starch into sugar, itself disappears. The action is not fully understood, but there is no doubt that when seeds germinate, the starch they contain is in this manner rendered soluble, and conveyed, as sugar, to all parts of the plant, there to be converted into woody fibre by a process the inverse of that by which woody fibre is converted into sugar. This latter is seen in the ripening of fleshy fruits, where a quantity of cellular matter (lignine) disappears, and the proportion of sugar very much increases.

VINOUS OR ALCOHOLIC FERMENTATION.

This name is given to that change by which sugar is resolved into alcohol and carbonic acid, by contact with a ferment. The sugar must be dissolved in water, and the solution must be exposed to a temperature of from 40° to 86° . If a ferment, such as yeast, be added, the sugar soon disappears, carbonic acid is given off in large quantity, and the liquid is found to contain alcohol, which may be separated by distillation. Now, grape sugar, $C_{12}H_{22}O_{11}$, contains the elements of 2 eq. alcohol, 4 eq. carbonic acid, and 2 eq. water, $2(C_4H_8O_2) + 4CO_2 + 2H_2O$; and, by very exact experiments it has been proved that 100 parts of grape

sugar yield only 47·12 of alcohol, 44·84 of carbonic acid, together 91·96 parts, the loss, 9·04 parts, being the 2 eq. of water separated. On the other hand, cane sugar, $C_{12}H_{22}O_{11}$, requires the addition of 1 eq. of water to yield 2 eq. alcohol, and 4 eq. carbonic acid, $= 2(C_4H_8O_2) + 4CO_2$; and here also experiment has demonstrated that 100 parts of cane sugar yield 53·727 parts of alcohol and 51·298 of carbonic acid, together 105·025; the increase, or 5·025 parts being due to the 1 eq. of water taken up to form dry grape sugar, $C_{12}H_{22}O_{12}$, into which cane sugar is converted before it undergoes fermentation. These facts prove that the ferment takes no direct part in the reaction, but only acts by inducing a state of change.

A considerable number of substances, if in a state of decomposition, act as ferments on a solution of sugar; among these are, besides yeast, vegetable gluten, albumen, caseine or fibrine, and the corresponding animal substances; also animal matter generally, if in a state of putrefaction.

The only explanation we can give is that the particles of these bodies, being in a state of decomposition, are in motion, and by communicating, mechanically, an impulse or motion to the particles of the sugar, destroy the balance of affinities to which the existence of sugar is owing; and thus give rise to a new balance or equilibrium, more stable under the given circumstances. The elementary particles of the sugar being disturbed in their previous arrangement, group themselves according to their individual affinities; and while the carbon forms, on one side, a compound containing all the hydrogen (alcohol), it yields on the other, a compound containing the greater part of the oxygen (carbonic acid).

When a natural juice, as that of the grape, ferments, some of the various substances it contains undergo a decomposition, probably of an analogous kind, giving rise to other new products, which are important in regard to the flavor of the liquid (wine, beer, or spirits), produced in the fermentation. Thus all wine contains œnanthic ether; potato spirit contains the oil of potato spirit (*Fussloel*, German); grain spirit contains a similar oil. It is not improbable, that besides the vinous fermentation which takes place in the greater part of the sugar, a peculiar reaction occurs, between a portion of the sugar and the ferment (or some other nitrogenized compound present), the result of which is the production of these peculiar oily liquids. The bouquet, or so much prized flavor of the finer wines, is doubtless owing to some ethereal compound produced in a similar way, but the origin, properties, and composition of which are as yet altogether unknown. It may be mentioned here, however, that œnanthic ether, which is the cause of that peculiar smell which belongs to all wine, and is so marked that we can at once tell, after many weeks or months, that an empty bottle has formerly contained wine, is a compound of oxide of ethyle

with a fatty acid ; and the oil of potato spirit is a compound analogous to alcohol, the hydrated oxide of a radical amyle, $C_{10}H_{21}$.

LACTIC FERMENTATION.

When a solution of sugar is placed in contact with pressed curd, or unsalted skimmed-milk cheese, which has previously been exposed to the atmosphere for some time, and the mixture is kept at a temperature from about 75° to 90° , a peculiar change takes place, which has been called a fermentation, but which differs from the vinous fermentation in this, that the escape of gas does not appear to be essential to it. The liquid soon becomes acid, from the conversion of sugar into lactic acid ; but when the amount of free acid reaches a certain point, the fermentation is thereby checked. If now the free acid be neutralized by the addition of carbonate of soda, or carbonate of lime (chalk), lactate of soda or of lime is formed, carbonic acid is disengaged, and the fermentation recommences. By repeating the addition of soda or chalk as often as free acid appears, the whole of the sugar may be at last converted into lactic acid, and obtained in the form of lactate of soda or of lime.

The best method is to dissolve 1 part of cane sugar or sugar of milk in about 5 of water, to add at the commencement $\frac{1}{2}$ part of prepared chalk, and a proper quantity of curd or cheese, and to place the whole in a temperature of 77° to 90° . Effervescence occurs, owing to the decomposition of the chalk, and in process of time the lactate of lime is deposited in small round masses of minute crystals, in such quantity as to solidify the whole mixture. This result sometimes takes place in ten days ; at other times, according to the precise temperature or the state of the curd, not till after several weeks or even months. But when it is complete, which is known by the cessation of the disengagement of gas and the solidification of the mass, the sugar appears to be entirely converted into lactic acid, without the formation of any other product. This is the true lactic fermentation ; but, as we shall see, it is apt to be mixed and complicated with other forms of decomposition.

The conversion of sugar, $C_{12}H_{22}O_{11}$, or of lactine, $C_{12}H_{22}O_{11}$, into lactic acid, $C_6H_8H_5HO$, or, $C_6H_{10}O_5 \cdot 2H_2O$, is very simple ; for lactine already contains the elements in the necessary proportion, and cane sugar requires only the addition of 1 eq. of water. It is therefore probable, *à priori*, that no other product should be formed along with the lactic acid ; and in several of my own experiments, I have obtained so large a quantity of lactate of lime as to lead to that conclusion, while I could detect no other product, except some coloring matter and a little undecomposed sugar.

It is this fermentation which occurs in milk when exposed to the air. The caseine enters into the state in which it becomes

capable of exciting the lactic fermentation in the sugar of milk (lactine); but as soon as the liquid becomes very acid, the fermentation is checked, unless an alkali be added. Hence sour milk contains both lactic acid and undecomposed lactine; but by the occasional addition of alkali the whole lactine may be converted into lactic acid, or rather, lactate of soda.

VISCOUS FERMENTATION.

When certain saccharine juices, such as those of beet-root, carrots, onions, &c., are exposed to a temperature of from 86° to 104° , a peculiar fermentation takes place. The sugar disappears, but instead of alcohol and carbonic acid, there are obtained mannite, lactic acid, and a mucilaginous substance, having the composition of gum; this latter renders the liquid ropy and viscid: hence the name given to the process.

The composition of mannite is	$C_5 H_7 O_5$
That of lactic acid is	$C_5 H_5 O_5$

Together	$C_{10} H_{12} O_{11}$
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It is evident, therefore, that 1 eq. of dry grape sugar, $C_{12} H_{22} O_{11}$, losing 1 eq. oxygen, might give rise to mannite and lactic acid. The gum has the same composition as sugar, so that we are led to believe that the nitrogenized constituents of the juice are acted on by the sugar, from which they obtain oxygen; and that these compounds are themselves decomposed by the oxygen, mannite, and lactic acid, which are very permanent, being produced from the sugar.

There is every reason to believe that the viscous fermentation is a mixed process, consisting of the lactic fermentation and of another, the true viscous fermentation, the products of which are gum and mannite. In the preparation of lactic acid from sugar, with the aid of curd as above described, I have sometimes obtained a little mannite, but always in so small a proportion as to indicate that its production was not essentially connected with that of the lactic acid, while in other experiments no mannite appeared. Where mannite did occur, I am inclined to suppose that the lactic fermentation was more or less complicated with the viscous.

BUTYRIC FERMENTATION.

After the sugar, in the lactic fermentation, has been converted as above described, into lactate of lime, if the mixture, still containing the caseine or curd, be kept for some time in a temperature of from 90° to 105° , the nearly solid mass of lactate dissolves by degrees, while a mixture of hydrogen and carbonic acid gases is given off, and at last the whole mass, except the cheese and any excess of chalk, becomes liquid. When the disengagement of gas has ceased, the liquid is found to contain no lactate, but only butyrate of lime; and this salt may be thus easily

obtained in any quantity. The conversion of lactic into butyric acid is easily explained; for $2 \text{ C}_6 \text{ H}_8 \text{ O}_6 = \text{C}_6 \text{ H}_8 \text{ O}_4 + \text{H}_2 +$

Lactic Acid. Butyric Acid.

4 CO_2 ; and it is probable that no other product is formed; for in some experiments I have seen the lactate converted entirely into pure butyrate of lime, which crystallized to the last drop.

It is evident that under certain circumstances the three kinds of fermentation just described may occur simultaneously, so that the liquid may contain lactic acid, butyric acid, mannite, gum, and unchanged sugar.

Mannite, $\text{C}_6 \text{ H}_7 \text{ O}_6$, occurs as the chief ingredient of manna. It is also found in certain juices, in mushrooms, in roots, such as that of celery, and is formed artificially as above described. It is easily purified by solution in alcohol and crystallization. It forms, when crystallized in water, large prisms, of a weak sweet taste. It is not susceptible of the vinous fermentation. Nitric acid and permanganate of potash act on it as on sugar. Concentrated arsenic acid gives it a brick-red color.

Lactic acid, $\text{C}_6 \text{ H}_8 \text{ O}_6 + \text{H}_2 \text{ O}$, so called because it occurs in sour milk, is also formed abundantly, as above described, in a peculiar fermentation of certain saccharine juices at a high temperature. In milk it is derived from the sugar of milk; and by neutralizing sour milk with carbonate of soda, adding sugar of milk, allowing it again to become acid, again neutralizing, and so on in succession, as long as the caseine causes the peculiar change to take place, it may be obtained in large quantity. A still easier process is to dissolve 14 parts of cane sugar in 60 of water, and to add 4 of moist cheese and 7 of prepared chalk. The mixture being kept some time at from 77° to 86° F. , will at last become quite thick with crystals of lactate of lime. If the action of the caseous ferment be pushed farther, and at a higher temperature, the lactate of lime is not obtained, but in its place, butyrate of lime in large quantity. (See Butyric Fermentation.) The above quantities will yield about 13 parts of lactate after it has been purified by crystallization; besides from $1\frac{1}{2}$ to 2 parts of mannite. The acid of sour crout is lactic acid, and by boiling the juice of sour crout with chalk or carbonate of zinc, lactate of zinc or of lime may be obtained.

Liebig has lately shown that lactic acid exists abundantly in the juice of flesh; and, as abundantly in the flesh of carnivorous as in that of herbivorous animals. This is remarkable, as the food of carnivorous animals contains no saccharine or amylaceous matter, so that the lactic acid must be formed from albuminous compounds. The same remark applies to the occurrence of lactine in the milk of the carnivora.

It has been stated by Cap and Henry, that lactic acid exists in normal urine, as lactate of urea; but I have never been able, by

their process to obtain from urine a trace of lactic acid, nor anything but pure urea. Pelouze and others were equally unsuccessful; and Liebig has proved by experiments on a very large scale, that urine contains no lactic acid in the normal state; and farther, that lactic acid, taken internally, cannot be recognized in the urine.

From the lactate of lime, lactic acid may be obtained by the action of oxalic acid, which removes the lime as oxalate. The filtered solution is lactic acid, which is concentrated by evaporation, and purified by solution in ether. From the lactate of soda, lactate of zinc may be obtained, by adding chloride of zinc to the hot saturated solution; on cooling, lactate of zinc, being sparingly soluble in cold water, crystallizes. This salt, acted on by barytic water, yields lactate of baryta, from which sulphuric acid removes the baryta, and the filtered liquid is pure diluted lactic acid.

In its most concentrated form, hydrated lactic acid is a syrupy liquid, of a very strong but pleasant acid taste. Its Sp. G. is 1.215. Its formula, $C_3H_5O_5 + H_2O = C_3H_7O_6$; but according to Engelhardt and Maddrell, it is bibasic, $C_{12}H_{10}O_{10}, 2H_2O = C_{12}H_{12}O_{12}$. It is therefore polymeric with dry grape sugar and with gum; both of which are $C_{12}H_{12}O_{12}$. At 482° the hydrate is decomposed, and yields a solid crystalline sublimate, $C_3H_4O_4$, which has been called anhydrous lactic acid, or sublimed lactic acid. This compound dissolves readily in hot water, and the solution if evaporated yields the original hydrate, $C_3H_7O_6 = C_3H_4O_4 + 2H_2O$. But when the acid is neutralized by bases, only one of the 2 eq. water taken up by the sublimed acid is replaced by a base; and consequently we cannot look on the sublimed acid as the true anhydrous acid. The anhydrous acid as it exists in the lactates, is $C_3H_5O_5$; and the sublimed acid is not lactic acid, but is converted into lactic acid when boiled with water.*

The general formula for the lactates is $C_3H_5O_5, MO$; or $C_{12}H_{10}O_{10}, 2H_2O$. The lactates of the alkalies are very soluble and deliquescent: that of lime is less soluble in cold water, and crystallizes readily. The lactate of zinc is sparingly soluble in cold water, and is hence well adapted for the extraction and purification of the acid.

XIX. METHYLE. $C_2H_3 = Mt$.

This is the hypothetical radical of a numerous series of compounds, entirely analogous to those of ethyle. There is the oxide of methyle, MtO , analogous to the oxide of ethyle; and the hydrated oxide of methyle, MtO, H_2O , analogous to alcohol. This last

* By distilling lactic acid with sea-salt, peroxide of manganese, and sulphuric acid, M. Stödler has produced aldehyde and chloral. If the quantity of chlorine is small, the aldehyde is produced in greatest quantity. S.

is the compound from which all the others are obtained. The extraordinary analogy between ethyle and methyle will enable us to describe the compounds of the latter very briefly.

1. HYDRATED OXIDE OF METHYLE. MtO, HO .

SYN. Pyroxilic Spirit. — This compound is one of the chief products of the destructive distillation of wood, and is found in the watery portion along with acetic acid, acetone, acetate of oxide of methyle, and several other ethereal liquids, besides portions of the oily matter of the tar dissolved in them.

By rectification with chloride of calcium, the pyroxilic spirit, which combines with that salt, is separated from several other liquids which distil over in the heat of the vapor bath. The residue, if mixed with its own bulk of water, and again heated in the vapor bath, now gives off the pyroxilic spirit, which is still mixed with water. It is purified by rectification with quicklime, which also destroys any acetate of methyle which may be present.

Pure hydrated oxide of methyle is a liquid very similar to alcohol, having the same density and the same degree of inflammability. Its odor is peculiar and ethereal. It boils at about 140° or 150° .

When heated with peroxide of manganese, water and sulphuric acid, it yields various products, among which, the chief are, formic acid, and formomethylal. It is decomposed by nitric acid, yielding oxalic acid, and by chlorine, yielding new products. It dissolves resins, and is used in making varnishes. It forms with baryta a crystalline compound, $BaO + MtO, HO$; and with chlorine of calcium, another crystalline body, in large hexagonal tables, $CaCl + 2(MtO, HO)$.

By the action of platinum powder, pyroxilic spirit is oxidized into formic acid, which bears the same relation to it that acetic acid does to alcohol.

2. OXIDE OF METHYLE. $MtO = (C_2H_3)O$.

This compound is obtained, like ether, (oxide of ethyle), when the preceding compound is distilled with its own volume of oil of vitriol; it escapes as an inflammable gas. Like oxide of ethyle, it is a base, and neutralizes acids. It even forms a neutral sulphate, which oxide of ethyle cannot do. It is worthy of notice, that oxide of methyle is polymeric with alcohol; for $C_4H_5O_2 = 2(C_2H_3O)$: so that these two bodies have the same composition, in 100 parts; that is, the same relative proportions of the same elements, but a very different absolute amount; the equivalent of alcohol being twice as heavy as that of oxide of methyle. The constitution of these compounds, moreover, is different, for one is a hydrate, $C_4H_5O + HO$; while the ether is an anhydrous oxide, C_2H_3O .

3. *Chloride of Methylene*, $C_2H_2, Cl = Mt\ Cl$ — Is a gas, of an ethereal smell, inflammable, of Sp. G. 1.1737. It is formed by the action of sulphuric acid and chloride of sodium on pyroxilic spirit. By the action of chlorine, aided by the sun's rays, it yields several new compounds containing chlorine.

4. *Iodide of Methylene*, $C_2H_2, I = Mt\ I$, — Is obtained by distilling 12 parts of pyroxilic spirit, 8 of iodine, and 1 of phosphorus. It is a liquid, boiling between 102° and 122° . The fluoride and cyanide of methyle are analogous liquids.

5. *Sulphide of Methylene*, $C_2H_2, S = Mt\ S$, — Is best formed by the action of a current of chloride of methyle on sulphide of potassium dissolved in alcohol: $Mt\ Cl + K\ S = Mt\ S + K\ Cl$. It is a mobile liquid, of a very offensive alliaceous odor, boiling at 104° . Its Sp. G. in the liquid form is 0.845; in the form of vapor, it is 2.115. With chlorine, it gives rise to several new compounds. The hydrosulphide of sulphide of methyle (corresponding to mercaptan) I obtained by distilling the double sulphate of methyle and potash with the hydrosulphide of sulphide of potassium: $(K\ O, Mt\ O, 2\ S\ O_2) + H\ S, K\ S = 2\ (K\ O, S\ O_2) + H\ S, Mt\ S$. Its formula is $H\ S, Mt\ S = C_2H_2, S + H\ S$. It is a colorless liquid, lighter than water, which boils at 70° , and acts on the oxides of mercury and lead exactly as mercaptan does. Its odor is most offensive, resembling that of leeks highly concentrated.

SALTS OF OXIDE OF METHYLE.

1. *Neutral Sulphate*, $Mt\ O, S\ O_2$, — Is obtained when pyroxilic spirit is distilled with a large excess of sulphuric acid. It forms an oily liquid, of a slightly alliaceous smell. It boils at 370° . Boiling water decomposes it into acid sulphate and hydrate of oxide of methyle. When heated with chlorides, cyanides, &c., it yields the compound of methyle, with chlorine, cyanogen, &c.; with a salt of benzoic, succinic, or other organic acid, it yields benzoate, &c. of oxide of methyle. Ammonia converts it into sulphamethylene.

2. *Bisulphate of Oxide of Methylene*. *SYN. Sulphomethylic Acid*, $H\ O, Mt\ O, 2\ S\ O_2$, — Is perfectly analogous to sulphovinic acid, and forms double salts, such as that of potash, $K\ O, Mt\ O, 2\ S\ O_2$, which are often called sulphomethylates, and correspond exactly to the sulphovinates. The acid sulphate itself may be obtained in crystals, which are very soluble and very acid. It is best obtained by the action of hot water on the neutral sulphates. The double salts, or sulphomethylates, are of no particular importance. They crystallize readily.

3. *Nitrate of Oxide of Methylene*, $Mt\ O, N\ O_2$, — Is obtained when pyroxilic spirit is distilled with nitrate of potash and sulphuric acid. It is an oily liquid, the vapor of which if heated beyond 248° explodes violently.

The neutral carbonate of methyle is not known; but double carbonates, analogous to those of ethyle with alcalies, may be prepared in the same way as those compounds.

4. *Oxalate of Oxide of Methyle*, $\text{Mt O}, \text{C}_2 \text{O}_3 = \text{C}_4 \text{H}_2 \text{O}_4$, — Is obtained in a manner analogous to that in which oxalic ether is prepared. It forms a crystalline solid, soluble in alcohol and pyroxilic spirit, which deposits it in large crystals. By the action of dry ammonia, it is converted into oxamethylene (analogous to oxamethane), which is the oxamate of oxide of methyle, $\text{C}_6 \text{H}_8 \text{N O}_5 = \text{C}_2 \text{H}_2 \text{O} + \text{C}_4 \text{H}_2 \text{N O}_5$. Liquid ammonia converts it into oxamide, as is the case with oxalic ether, only here pyroxilic spirit and not alcohol is formed at the same time: $\text{C}_2 \text{H}_2 \text{O}, \text{C}_2 \text{O}_3 + \text{N H}_3 = \text{C}_2 \text{H}_2 \text{O}, \text{H O} + \text{C}_2 \text{O}_3 \text{N H}_2$. This is perhaps the easiest way of obtaining oxamide in large quantity.

Bisulphide of carbon and hydrated cyanic acid act on pyroxilic spirit exactly as on alcohol, producing analogous compounds.

5. *Benzoate of Oxide of Methyle*, $\text{Mt O}, \text{Bz O}_2$, — Is best obtained by distilling dry benzoate of lime or soda with neutral sulphate of methyle. It is an oily liquid of a balsamic odor, analogous in other respects to benzoic ether.

6. *Acetate of Oxide of Methyle*, $\text{Mt O}, \text{Ac O}_2$, — Is obtained in the same way as acetic ether, which it resembles. It occurs in considerable quantity in raw pyroxilic spirit, and even in that which has only been purified by rectification. When quick-lime is used in the rectification, it is destroyed, yielding an additional quantity of the pure hydrate of oxide of methyle. It is very volatile and inflammable, and for most purposes its presence in the wood spirit is not at all injurious. It is isomeric with formiate of oxide of ethyle; for $\text{C}_2 \text{H}_2 \text{O} + \text{C}_4 \text{H}_2 \text{O}_2 = \text{C}_4 \text{H}_2 \text{O} + \text{C}_2 \text{H O}_2$.

7. *Salicylate of Oxide of Methyle*, — Exists ready formed, as the volatile oil of *gaultheria procumbens*, or wintergreen. It is very fragrant, and plays the part of an acid, combining with alcalies. When heated with them, however, salicylates are formed, and pyroxilic spirit set free. It is a very interesting compound, as it contains two substances, previously only known as artificial products; namely, salicylic acid and oxide of methyle. It is acted on by nitric acid and other re-agents exactly in the same way as the salicylate of oxide of ethyle, (which see.)

The mucate of oxide of methyle is a crystalline solid, analogous in its preparation and properties to the corresponding salt of ethyle.

The action of chlorocarbonic acid on pyroxilic spirit is exactly analogous to its action on alcohol, producing an oily liquid, $\text{C}_4 \text{H}_2 \text{Cl O}_4 = \text{C}_2 \left\{ \begin{array}{l} \text{O}_2 \\ \text{Cl} \end{array} \right. + \text{C}_2 \text{H}_2 \text{O}$. By the action of ammonia, this liquid produces a compound, urethylane, (corresponding to ure-

thane) $C_4 H_5 N O_4$ or $C_2 H_{10} N_2 O_3 = C_2 H_4 N_2 O_2 + 2 (C_2 H_3 O, CO_2)$; that is, a compound, possibly, of 1 eq. urea, with 2 eq. neutral carbonate of methyle, but more probably of carbamic acid, $CO_2, CONH_2$, and oxide of methyle, $C_2 H_3 O$.

When a current of ammonia is made to act on the neutral sulphate of methyle, there is produced a crystalline compound, $C_2 H_5 N S_2 O_6$, which has been called sulphamethylane, and may be viewed as oxamethylane, in which sulphamide, $SO_2 NH_2$, has been substituted for oxamide, $C_2 O_2 NH_2$; or SO_2 for $C_2 O_2$. It may also be considered, if oxamethylane be the oxamate of oxide of methyle, $C_2 H_3 O + C_4 H_2 N O_5$, as composed of oxide of methyle and a peculiar acid, formed of hyposulphuric acid and amide, or rather of sulphuric acid and sulphamide, and which may be called sulphamic acid; and its formula will be $C_2 H_3 O + (S_2 O_2, NH_2)$, or $C_2 H_3 O + (SO_2 + NH_2, SO_2)$. On this view, sulphamethylane is the sulphamate of oxide of methyle.

When hydrated oxide of methyle is oxidized by means of platinum powder, it is finally converted into pure formic acid. There is evidently, therefore, the same relation between methyle and formic acid, as between ethyle and acetic acid; and on comparing the formulæ of pyroxilic spirit and of formic acid, $C_2 H_3 O, HO$, and $C_2 H O_2, HO$, we perceive that the former, to be converted into the latter, must have lost 2 eq. hydrogen, and taken up 2 eq. oxygen. This is exactly what takes place with alcohol, and there can be no doubt, that the pyroxilic spirit yields an intermediate compound, exactly analogous to aldehyde, although this has not yet been isolated. Such a compound would be the hydrated protoxide of a derived radical, formyle, analogous to acetylene, of which formic acid is the hydrated peroxide; and its formula would be $(C_2 H) O + HO$. We shall therefore, assume the existence of this radical, and proceed to describe its compounds, which are analogous to those of acetylene.

XX. FORMYLE. $C_2 H = Fo$.

This radical is unknown in a separate form, as are its protoxide and deutoxide, corresponding to aldehyde and aldehydic acid. But when hydrated oxide of methyle is distilled with sulphuric acid, water, and peroxide of manganese, a volatile liquid is obtained, which is a mixture of formiate of oxide of methyle, and another liquid called methylal. When purified, this latter has the formula $C_2 H_5 O_4$, which indicates, that it is composed of $C_2 HO, HO$, or hydrated oxide of formyle, and 2 eq. of oxide of methyle, $2 (C_2 H_3 O)$. This compound, briefly, $Fo O. HO + 2 MtO$, corresponds to acetal in the series of ethyle; acetal being $AcO, HO + AeO$.

Formic Acid. $C_2 H O_2, HO = Fo O_2 H O$.

This remarkable acid occurs in the red ant, *formica rufa*, and may be obtained, in a diluted and impure state, by infusing these

insects in water. Its production from pyroxilic spirit has been described above. It may also be prepared by distilling a mixture of starch or sugar with peroxide of manganese, water, and sulphuric acid: and it is formed under a great variety of circumstances from many organic compounds.

To prepare the hydrated acid pure and concentrated, the dry formiate of lead, Pb O , Fo O_2 , is decomposed by sulphuretted hydrogen gas, and the vapor of the formic acid, condensed in a well-cooled receiver. It is boiled for a few moments to expel any sulphuretted hydrogen. It is a clear liquid, of Sp. G. 1.235, fuming slightly, and has a very pungent acid smell. Below 32° it crystallizes in brilliant scales. It boils at 212° , and its vapor is inflammable, burning with a blue flame. This is probably owing to the formation of carbonic oxide, for the acid $\text{C}_2 \text{H O}_2$, H O , contains the elements of 2 eq. carbonic oxide, $\text{C}_2 \text{O}_2$, and 2 eq. water, $\text{H}_2 \text{O}_2$.

With 1 eq. of water, it forms the second hydrate, $\text{Fo O}_2 + 2 \text{H O}$, which much resembles the first in properties. Its boiling point is 221° , and its Sp. G. is 1.110.

Both these hydrates are highly corrosive; a drop of either on any delicate portion of the skin causes a severe burn, which blisters, suppurates, and is very painful and difficult to heal. In this respect the formic acid can only be compared to hydrofluoric and hydrated cyanic acids.

A weaker acid is obtained by distilling formiate of soda, lime or lead, with sulphuric acid, previously diluted with half its weight of water. Ten parts of formiate of lime, 8 of oil of vitriol, and 4 of water, yield 9 of formic acid, of Sp. G. 1.075.

The salts of the acid are best prepared from the weak and impure acid, obtained by distilling a mixture of 10 parts of starch, 37 of peroxide of manganese, 30 of oil of vitriol, and 30 of water. These materials yield 3.35 parts of formic acid, such that 100 parts neutralize 15 of dry carbonate of soda. From this acid, the formiate of lead may be easily prepared and purified; and from it, by the addition of carbonate of soda, formiate of soda may be obtained.

Formic acid is easily recognized by the action of sulphuric acid, which decomposes, without blackening, both it and its salts, causing the disengagement of pure carbonic oxide. It also reduces the oxides of all the noble metals, and is itself oxidized into carbonic acid. Formic acid not only reduces the oxides, but also in most cases, the soluble salts of the noble metals. 1 eq. formic acid can reduce 2 eq. of a protoxide, such as that of silver, $2 \text{Ag O} + \text{C}_2 \text{H O}_2 = \text{Ag}_2 + \text{H O} + 2 \text{C O}_2$; or 1 eq. of a deutoxide, such as that of mercury; $\text{Hg O}_2 + \text{C}_2 \text{H O}_2 = \text{Hg} + \text{H O} + 2 \text{C O}_2$.

Formic acid is a very powerful acid, and forms salts with bases, all of which are soluble. They are generally similar to the

acetates, but yet quite distinct. Many metallic formiates when heated in close vessels give off carbonic acid and carbonic oxide, leaving the metal reduced ; others give off carbonic oxide, leaving the oxide.

Formiate of ammonia, $\text{NH}_4 \text{O}$, $\text{C}_2 \text{H O}_2$, contains the elements of hydrocyanic acid and water, $\text{C}_2 \text{NH} + 4 \text{H O}$; and is converted into these compounds when its vapor is passed through a red-hot tube. Formiate of oxide of ethyle, prepared like the acetate, is a volatile ethereal liquid with a peculiar aromatic smell. The corresponding salt of oxide of methyle is quite analogous. Formiate of potash is very deliquescent. Formiate of soda is also very soluble, but may be obtained in crystals. It is a very powerful reducing agent, both in a moist and dry way. In the former, it reduces the noble metals, in the latter, at a red-heat, by virtue of the carbonic oxide it gives off, it reduces most of the reducible metals, such as lead, copper, antimony, arsenic, cobalt, nickel, &c. Formiate of lead is sparingly soluble in cold water, and is, therefore, easily purified, and serves to prepare formic acid and formiate of soda. Formiate of deutoxide of mercury and formiate of protoxide of mercury, both exist. When red oxide of mercury is dissolved in cold formic acid, the former salt is produced ; but the slightest heat causes an effervescence, while formiate of the protoxide is deposited in silvery scales like the acetate. These when warmed are decomposed with effervescence and deposition of metallic mercury. Formiate of silver resembles the acetate, but is very easily decomposed by heat, the metal being reduced.

COMPOUNDS OF FORMYLE WITH CHLORINE, ETC.

When chlorine or hypochlorites act on oxide of methyle, hydrated oxide of methyle, and chloride of methyle, a great variety of new compounds are produced, corresponding in most cases to the compounds obtained by the action of chlorine, &c., on alcohol, ether, and chloride of ethyle. Our space forbids us to give the details of these compositions ; but we may mention that two of the compounds formed by the action of chlorine on the compounds of ethyle and acetylene, may be viewed as protochloride and bichloride of formyle. These are $\text{C}_4 \text{H}_2 \text{Cl}_2 = 2 (\text{C}_2 \text{H, Cl})$, and $\text{C}_4 \text{H}_2 \text{Cl}_4 = 2 (\text{C}_2 \text{H, Cl}_2)$. The perchloride of formyle, $\text{Po Cl}_3 = \text{C}_2 \text{H, Cl}_3$, is also produced from a compound of the ethyle series, namely from chloral, by the action of alkalies. It is an oily liquid of a sweet taste and ethereal smell. * When acted on

* This substance is now termed *chloroform*, and is used as an anæsthetic agent. Since the London edition of this work went to press, Prof. Gregory, has examined chloroform with regard to its purity. Most of the commercial article is impure, but may be easily purified, according to Prof. Gregory, by agitating it with pure sulphuric acid, and allowing the liquids to remain in contact, for some time, with occasional agitation. Half the volume of acid

by alcalies, it yields chlorides and formiates; thus with potash, $C_2 H Cl_3 + 4 K O = 3 K Cl + K O, C_2 H O_3$.

When acted on by chlorine, perchloride of formyle yields perchloride of carbon, $C_2 Cl_4 = C_2 Cl, Cl_2$, just as perchloride of acetylene, $C_4 H_2, Cl_2$, yields sesquichloride of carbon, $C_4 Cl_3 = C_4 Cl_2, Cl_2$.

Perbromide of formyle is obtained from bromal. Periodide of formyle, obtained by the action of alcohol on iodine and potash, is a yellow crystalline, volatile solid, having an odor analogous to that of saffron.

When chlorine acts on oxide of methyle, $C_2 H_2 O$, it produces, by substitution of chlorine for hydrogen, the compounds $C_2 \begin{Bmatrix} H_2 \\ Cl \end{Bmatrix} O$; $C_2 \begin{Bmatrix} H \\ Cl_2 \end{Bmatrix} O$; and finally, $C_2 Cl_2, O$. The second may be considered as formic acid, $C_2 H O_2$, in which two-thirds of the oxygen are replaced by chlorine, $C H \begin{Bmatrix} O \\ Cl_2 \end{Bmatrix}$. It will then be an oxychloride of formyle, analogous to oxychloride of acetylene.

When chlorine acts on chloride of methyle, $C_2 H_2 Cl$, three compounds are formed by substitution. These are, 1st, $C_2 H_2 Cl_2 = C_2 \begin{Bmatrix} H_2 \\ Cl \end{Bmatrix} Cl$; 2d, perchloride of formyle, $C_2 H Cl_3 = C_2 \begin{Bmatrix} H \\ Cl_2 \end{Bmatrix} Cl$; and 3d, as before explained, perchloride of carbon, $C_2 Cl_4 = C_2 Cl_2, Cl_2$.

The action of chlorine on sulphide of methyle, $C_2 H_2 S$, appears to yield, $C_2 \begin{Bmatrix} H_2 \\ Cl \end{Bmatrix} S$; $C_2 \begin{Bmatrix} H \\ Cl_2 \end{Bmatrix} S$; and $C_2 Cl_2 S$.

The action of chlorine on oxalate, benzoate, and acetate of oxide of methyle is quite analogous to its action on the corresponding compounds of ethyle, producing the oxalate, benzoate, and acetate of oxychloride of formyle, $C_2 O_2 + C_2 H \begin{Bmatrix} O \\ Cl_2 \end{Bmatrix}$; $C_6 H_5 O_2 + C_2 H \begin{Bmatrix} O \\ Cl_2 \end{Bmatrix}$; and $C_4 H_3 O_2 + C_2 H \begin{Bmatrix} O \\ Cl_2 \end{Bmatrix}$. These curious results, like those which precede them, are here merely indicated, as we have explained the principle of their formation under the heads of ethyle and acetylene.

In some specimens of raw pyroxilic spirit there occurs a large proportion of a peculiar volatile liquid, which has been called lignone or xylite. As its constitution is quite uncertain, although it

will be sufficient. If the acid should be considerably colored, a second quantity should be used, otherwise not. The purification is then finished with peroxide of manganese, with which it is to be agitated and left in contact until the odor of sulphurous acid is removed. Pure chloroform should have a Sp. G. of 1.500, nor should any be used for anæsthetic purposes unless perfectly pure, as serious accidents are liable to occur from the use of the commercial article.

is believed to contain some compound of oxide of methyle, we shall state what is known of it when treating of the products of the dry distillation of wood.

XXI. CETYLE. $C_{31}H_{63} = Ct$.

This is the hypothetical radical of a series of compounds, derived from spermaceti. The principal one is ethal, the hydrated oxide of cetylc, analogous to alcohol.

Hydrated Oxide of Cetylc. $C_{31}H_{63}O, H O = Ct O, H O$.

SYN. Ethal.—This compound exists in spermaceti, in combination with cetylic or ethalic acid $C_{31}H_{61}O_2$. When spermaceti is digested with strong caustic potash, a soap is produced; and this being decomposed by sulphuric acid, yields a fatty mixture composed of cetylic acid and ethal. The whole is acted on by baryta, with which the acids unite; and the ethal is dissolved from the mixture by cold alcohol. It is afterwards purified by means of ether.

Ethal forms a white crystalline solid, like wax, fusible, about 118° , volatile at a higher temperature, soluble in alcohol. As above mentioned, it is analogous to alcohol; and although the oxide of cetylc has not yet been obtained in a separate form, yet there have been formed the chloride of cetylc, and the double sulphate of oxide of cetylc and potash, analogous to the corresponding compounds of ethyle.

When ethal is repeatedly distilled with anhydrous phosphoric acid, it loses the elements of 2 eq. of water, yielding a new compound, cetene $= C_{31}H_{62}$, analogous to olefiant gas or etherine. It is an oily inflammable liquid. Cetylic or ethalic acid will be hereafter described. Its formula is $C_{31}H_{61}O_2, H O = C_{31}H_{63}O_4$; it belongs to the series $(CH)_n + O_4$.

XXII. AMYLE. $C_{10}H_{21} = Ayl$.

This is the hypothetical radical of a series of compounds, derived from oil of potato spirit, which is itself, when pure, the hydrated oxide of amyle, analogous to alcohol. Both the radical and its anhydrous oxide are unknown in the separate state; but a sufficient number of compounds has been obtained to render its existence highly probable.

Hydrated Oxide of Amyle. $C_{10}H_{21}O, H O = Ayl O, H O$.

SYN. Oil of Potato Spirit; in German, *Fuselöl*.—This compound distils over toward the end of the first distillation of spirits made from potatoes, rendering these last portions of the spirit milky and very offensive. It separates on standing as an oily liquid, which is washed with water to remove alcohol, dried by chloride of calcium, and rectified till its boiling point becomes steady at 269° or 270° . It is then pure.

It is a colorless oily liquid, very mobile, of a strong and nauseous odor, which produces stupifying effects. Its vapor, when

inhaled, causes cough and spasmodic dyspnoea, resembling asthma, often followed by vomiting. Its taste is very acid and nauseous. Its Sp. G. is 0.812. At -4° it crystallizes in shining scales. When heated with dry hydrate of potash it is oxidized, hydrogen being given off, and the potash is found combined with valerianic acid, $C_{10}H_9O_2$. When distilled with anhydrous phosphoric acid, it yields a new carbohydrogen, amylene = $C_{10}H_{10}$.

The chloride of amyle has not yet been obtained; but the bromide and iodide are formed when the hydrated oxide is distilled along with phosphorus and bromine or iodine. They are both heavy oily liquids, and their formulæ are $Ayl\ Br$, and $Ayl\ I$.

The bisulphate of oxide of amyle or sulphamilic acid, $Ayl\ O, H\ O, 2\ S\ O_3$, is analogous to sulphovinic acid. With bases it forms double salts, the formula of which is $M\ O, Ayl\ O, 2\ S\ O_3$, which are soluble in water and crystallizable. The solutions, when boiled, yield hydrated oxide of amyle, free sulphuric acid, and a neutral sulphate.

The acetate of oxide of amyle is an ethereal liquid, analogous to acetic ether. Its formula is $C_{14}H_{14}O_4 = C_{10}H_{11}O, C_4H_3O_3 = Ayl\ O, Ac\ O_3$.

The hydrosulphide of sulphide of amyle, $Ayl\ S, H\ S$, is prepared in the same way as mercaptan, to which it is quite analogous. It is an oily liquid, boiling at 243° , of Sp. G. 0.835. It has, like the corresponding compounds of ethyle and methyle, a most penetrating odor of onions; and, like them, it acts on red oxide of mercury, forming a white crystalline compound, $Ayl\ S, Hg\ S$.

The sulphocarbonate of oxide of amyle, very analogous to the bisulphocarbonate of oxide of ethyle, is formed when bisulphide of carbon acts on a solution of potash in oil of potato spirit.

OXIDATION OF HYDRATED OXIDE OF AMYLE.

Valerianic Acid. $C_{10}H_9O_2, H\ O = C_{10}H_{10}O_4$.

It has already been mentioned, that when oil of potato spirit is heated with dry hydrate of potash, hydrogen is given off, and valerianate of potash is formed. Here the oil, $C_{10}H_{11}O, H\ O$, loses 2 eq. hydrogen, and gains 2 eq. oxygen; so that valerianic acid stands to amyle in the same relation as acetic acid to ethyle, and formic acid to methyle. The acid is easily separated by distilling the salt of potash with diluted sulphuric acid. In composition and in all its properties, it agrees with the native valerianic acid, obtained by distilling the root of *valeriana officinalis* with water. It belongs to the series of acids, the general formula of which is $(CH)_n + O_4$.

Valerianic acid is a limpid, oily fluid, of a disagreeable and peculiar smell. Its Sp. G. is 0.944, and it boils at 270° . With bases, it forms soluble salts, which have a sweet taste.

The action of chlorine on hydrated oxide of amyle gives rise to the formation of a compound, chloramilal, supposed to be analogous to chloral, but the composition and nature of which are not fully known.

Amilene, the carbohydrogen obtained by distilling hydrated oxide of amyle with dry phosphoric acid, has the formula $C_{10}H_{18}$, and is, like cetene, isomeric with olefiant gas.

XXIII. GLYCERYLE. $C_3H_7 = Gl$.

This is the hypothetical radical of glycerine, a basic compound which exists in all neutral fat oils combined with oily acids.

Hydrated Oxide of Glyceryle. $C_3H_7O_3 + H_2O = GlO_3, H_2O$.

Syn. *Glycerine*. — To obtain it, olive oil is converted into plaster by long boiling with litharge and water. When the plaster is completely formed, the glycerine is found dissolved in the water. It is purified from lead by sulphuretted hydrogen, and is then concentrated in the vapor bath and finally in vacuo. When pure, it forms a viscid syrup, colorless or slightly yellow. It has a decided sweet taste, and its Sp. G. is 1.252. By the action of heat it is decomposed, yielding a peculiar volatile compound, acroleine, which attacks the eyes most powerfully. This substance has lately been studied by Redtenbacher: we shall give his results when treating of the action of heat on fat oils.

With sulphuric acid, glycerine forms an acid sulphate, $C_3H_7O_3, H_2O, 2SO_3$; which forms double salts, analogous to the sulphovinates, the formula of which is, $M O, GlO_3, 2SO_3$.

There is reason to believe that the basic compound in oils has not the composition of the isolated glycerine. In some oils it would appear to be C_3H_2O , which Berzelius calls oxide of lipyle; and $C_3H_7O_3 = 2(C_3H_2O) + 3H_2O$. On this view, oxide of lipyle, when separated, combines with water to yield glycerine. We shall also see that acroleine, the product of the action of heat on glycerine, is $C_3H_4O_2 = 2(C_3H_2O)$.

Having now briefly described the known or admitted organic radicals and their derivatives, we proceed to consider the organic acids whose composition is known, although we cannot speak with certainty of their constitution, their radicals being yet unknown.

ORGANIC ACIDS.

1. CITRIC ACID. $C_{12}H_5O_{11}, 3H_2O = \overline{Ci}, 3H_2O$.

This acid is found in many vegetable juices, especially those of sour fruits, as the lemon, lime, orange, red-currant, &c. It is extracted by adding chalk to the acid juice, by which means an insoluble citrate of lime is formed. This is decomposed by diluted sulphuric acid with the aid of heat, and the solution, filtered from the sulphate of lime, gives on evaporation and cooling crystals of

citric acid, consisting of $\text{Ci}, 3 \text{H O} + \text{aq.}$ A slight excess of sulphuric acid promotes the crystallization.

It forms large transparent crystals, very soluble in water, of a very strong and agreeable acid taste. A diluted solution is soon decomposed, becoming mouldy. By spontaneous evaporation of a saturated solution, crystals may be obtained, which are $\text{Ci}, 3 \text{H O} + 2 \text{aq.}$ At 212° , these lose the 2 eq. of water of crystallization. The other crystals, above mentioned, do not lose water at 212° , but melt at 256° ; and when heated beyond 300° , both kinds are decomposed. Heated with oil of vitriol in excess, citric acid is decomposed, yielding,

From 1 eq. citric acid	$\text{C}_{12} \text{H}_8 \text{O}_{14}$
2 eq. carbonic acid	$\text{C}_2 \text{O}_4$
2 eq. carbonic oxide	$\text{C}_2 \text{O}_2$
2 eq. acetic acid	$\text{C}_4 \text{H}_6 \text{O}_6$
2 eq. water	$\text{H}_2 \text{O}_2$
	<hr/>
	$\text{C}_{12} \text{H}_8 \text{O}_{14}$

In like manner, when fused with caustic potash, citric acid is resolved into 2 eq. of acetic acid, 2 eq. oxalic acid, and 2 eq. water.

When citric acid is added to lime-water, the liquid remains clear, but when heated becomes turbid, and deposits citrate of lime. This character serves to distinguish citric acid from most other vegetable acids.

SALTS OF CITRIC ACID.

Citric acid is tribasic, and forms three series of neutral salts, that is, of salts with 3 eq. of base, whether fixed base or basic water. It also forms basic salts, of the formula $\text{Ci}, 3 \text{M O} + \text{M O}$ or $\text{Ci}, 3 \text{M O} + \text{M O} + \text{aq.}$ These basic salts correspond in constitution to the two forms of crystallized acid.

When a dry citrate, with 3 eq. of fixed base, is decomposed by an alcoholic solution of hydrochloric acid, so that no more water is presented to the citric acid than the 3 eq. of basic water derived from the hydrogen of the hydrochloric acid and the oxygen of the base, there are formed, from 3 eq. dry citric acid, 2 eq. of the acid with 1 eq. of water of crystallization, and 3 eq. of the hydrated acetic acid: $3 (\text{C}_{12} \text{H}_8 \text{O}_{14}, 3 \text{H O}) = 2 (\text{C}_{12} \text{H}_8 \text{O}_{14}, 3 \text{H O} + \text{aq.}) + 3 (\text{C}_4 \text{H}_6 \text{O}_6, \text{H O})$. This is the same change which takes place in citric acid when heated to a certain point, water being given off.

Citrate of oxide of ethyle, $\text{Ci}, 3 \text{Ac O}$, is an oily liquid of Sp. G. 1.142. By alcalies it is converted into citrates and alcohol.

Citrate of potash occurs in three forms : $\overline{\text{Ci}}, 3 \text{K O}$; $\overline{\text{Ci}}, \left\{ \begin{array}{l} 2 \text{K O} \\ \text{H O} \end{array} \right.$; and $\overline{\text{Ci}}, \left\{ \begin{array}{l} \text{K O} \\ 2 \text{H O} \end{array} \right.$. All are very soluble, and crystallize with difficulty.

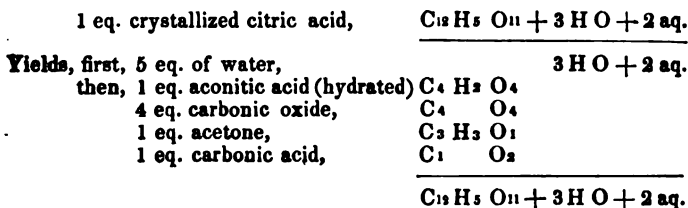
Citrate of soda also forms three salts. 1. $\overline{\text{Ci}}, 3 \text{Na O} + 11 \text{ aq.}$ This salt forms large regular crystals. 2. $\overline{\text{Ci}}, 2 \text{Na O}, \text{H O}$; formed by adding to a solution of the preceding salt half as much citric as it already contains. It forms by evaporation, needles of a very pleasant subacid taste. 3. $\overline{\text{Ci}}, \text{Na O}, 2 \text{H O}$. Formed by adding to a solution of No. 1, as much citric acid as it already contains. This salt does not crystallize in water, but forms a gummy mass. A saturated alcoholic solution, however, deposits crystalline grains.

Citrate of baryta forms two varieties. 1. $\overline{\text{Ci}}, 3 \text{Ba O} + 7 \text{ aq.}$ which falls when citrate of soda is added to chloride of barium. 2. $2 \overline{\text{Ci}}, \left\{ \begin{array}{l} 5 \text{Ba O} \\ \text{H O} \end{array} \right. + 7 \text{ aq.} = \overline{\text{Ci}}, \left\{ \begin{array}{l} 2 \text{Ba O} \\ \text{H O} \end{array} \right. + \overline{\text{Ci}}, 3 \text{Ba O} + 7 \text{ aq.}$ This is deposited on cooling, when a boiling solution of citrate of soda is added to a boiling solution of chloride of barium and free citric acid. Citrate of lime also yields two salts. 1. Neutral, $\overline{\text{Ci}}, 3 \text{Ca O} + 4 \text{ aq.}$ formed by mixing chloride of calcium and citrate of soda. It is insoluble. 2. Basic, $\overline{\text{Ci}}, 3 \text{Ca O} + \text{Ca O} + \text{aq.}$, formed when citric acid is heated with excess of lime-water. The citrate of lime formed from lemon, or currant juice, by chalk, is an impure mixture of the basic and neutral salts. Citrates of lead, 1. $\overline{\text{Ci}}, 3 \text{Pb O} + \text{aq.}$ 2. $\overline{\text{Ci}}, 2 \text{Pb O}, \text{H O} + 2 \text{ aq.}$: 3. Basic : $\overline{\text{Ci}}, 3 \text{Pb O} + 3 \text{Pb O}$. 4. Also basic. $\overline{\text{Ci}}, 3 \text{Pb O} + \text{Pb O} + \text{aq.}$ These are all sparingly soluble or insoluble, and are decomposed by washing. Citrate of copper is basic, $\overline{\text{Ci}}, 3 \text{Cu O} + \text{Cu O}$. Citrate of silver is a brilliant white, insoluble powder, $\overline{\text{Ci}}, 3 \text{Ag O} + \text{aq.}$ It loses its water under 80° . Citrate of antimony and potash is a double salt, $\overline{\text{Ci}}, \text{Sb}_2 \text{O}_3 + \text{Ci}, 3 \text{K O} + 5 \text{ aq.}$ It forms hard, brilliant, white prisms, which lose their water at 212° .

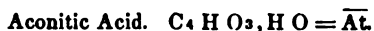
The *Ferro-citrate of Morphine*. — This double salt may be formed by adding to a saturated solution of citric acid, pure morphine; and then neutralizing with moist hydrated sesquioxide of iron. It forms a red salt which may be obtained in beautiful red scales, by evaporating the solution down to the consistence of syrup, pouring upon glass, and drying with a moderate heat. This salt will doubtless prove highly efficacious in medicine. The *Ferro-citrate of Salicine* can also be prepared by following the above process, substituting salicine for morphine. Salicine is a weak base, but will form salts with acids and acid radicals, under favorable circumstances. — (*Sanders.*)

ACTION OF HEAT ON CITRIC ACID.

The first effect of heat on crystallized citric acid is to melt it, and the next, to expel the water of crystallization. The acid, if now dissolved, crystallizes unchanged. But if the heat be continued, there is given off gas and inflammable vapors, and the residue is no longer citric acid, but hydrated aconitic acid.



When the heat is increased, other products appear, particularly two new acids. But these are derived from aconitic acid. They are itaconic and citraconic acids.



Syn. Equisetic Acid. — This acid occurs native in *aconitum napellus* and in *equisetum fluviatile*. It is formed by the action of heat on citric acid, as above. To obtain it, citric acid is heated till it ceases to give off inflammable vapors, and the residue, dissolved in alcohol, is treated with hydrochloric acid gas, which causes the formation of aconitic ether. The addition of water causes this to separate, and by caustic potash, it is converted into aconitate of potash. From this, aconitate of lead is prepared, and this salt, decomposed by sulphuretted hydrogen, yields the acid.

It forms indistinct crystals, and although the acid thus prepared has the same composition as that from aconite, and that from *equisetum*, yet each of the three varieties has some peculiarities. They may not, therefore, be identical, especially as two acids, derived from malic acid, the maleic and paramaleic, or fumaric acids, have the same composition. The aconitic acid from citric acid, when heated, yields itaconic and citraconic acids; it is doubtful, at present, whether the other two varieties do so.

Aconitic acid, according to the present state of our knowledge, is monobasic, and the general formula of its salts is $\overline{At}, M O$. The aconitates are not important.

When aconitic acid (from citric acid) is heated to from 356° to 392° , it boils and yields a mixture of two acids; itaconic acid, which condenses in crystals, and citraconic acid, which appears as an oily liquid. When the distillation is very rapid, itaconic acid predominates; when it is slow, there is more citraconic acid. These two acids have both the formula $C_4 H_2 O_3, H O$.

Itaconic acid is readily purified by solution in hot water, as it crystallizes with great facility. It is soluble in water, alcohol and ether. When heated it is resolved into water and anhydrous citraconic acid. It is a monobasic acid, and its formula is $C_5 H_2 O_3$, $H O = \bar{I}t$, $H O$. The formula of its salts is $\bar{I}t$, $M O$. It also forms acid salts, the formula of which is $2 \bar{I}t$, $M O$, $H O$. The itaconates are not of special interest.

Citraconic acid is formed when the preceding acid is distilled, and then appears in the anhydrous state, as a limpid oily liquid. It distils unaltered, at 410° , and volatilizes slowly at much lower temperatures. It attracts moisture from the air, forming a crystalline hydrate, which, when heated, is again resolved into water and anhydrous acid. The formula of the anhydrous acid is $C_5 H_2 O_3 = \bar{C}t$; that of the hydrate $\bar{C}t$, $H O$. It forms, like the preceding, both neutral and acid salts; and produces with oxide of silver, a neutral salt, with water of crystallization; an apparently anomalous case. The formation of these two acids takes place as follows: 3 eq. of aconitic acid, $3 (C_4 H_2 O_4)$, yield 2 eq. itaconic acid, $2 (C_5 H_2 O_3, H O)$ and 2 eq. carbonic acid, $2 C O_2$. The itaconic acid, when formed, is partially resolved into water and anhydrous citraconic acid.

The three acids just described, aconitic, itaconic and citraconic acids, require farther investigation. It is probable that it will be found that they are not all monobasic. The existence of water of crystallization in the neutral citraconate of silver is a most unusual circumstance, and would seem to indicate that we do not yet know the constitution of the acid in that salt.

2. TARTARIC ACID. $C_4 H_4 O_6, 2 H O = \bar{T}, 2 H O$.

This acid occurs in the juice of the grape as acid tartrate of potash; also in many other plants. It is prepared from tartrate of lime exactly as citric acid is from citrate of lime. Tartrate of lime is obtained by the action of chalk on acid tartrate of potash, or cream of tartar.

Tartaric acid crystallizes in large rhombic prisms, transparent and colorless. They are very soluble in water, and have a pleasant acid taste. When boiled with alcohol, tartaric acid forms acid tartrate of oxide of ethyle. A high temperature decomposes tartaric acid, giving rise to several new products.

An excess of potash aided by heat, transforms it into acetate and oxalate of potash, $C_4 H_4 O_6, 2 H O = C_4 H_2 O_3, H O + 2 (C_2 O_3 H O)$. By peroxide of manganese and sulphuric acid it is converted into formic acid, carbonic acid, and other products. There is some relation between tartaric and formic acids: for if formic acid be $Fo O_2$ ($Fo = C_2 H$), tartaric acid is $2 (Fo_2 O_2)$.

Tartaric acid precipitates lime-water white, but an excess dissolves the precipitate. In solution of potash, if the acid be added

in excess, it causes a crystalline deposit of cream of tartar, which, where the potash is in very minute proportion, is rendered more visible by the addition of alcohol.

It is a bibasic acid, and forms two series of salts: 1. Neutral, \bar{T} , 2 M O; 2. Acid, \bar{T} , M O, H O. It forms also two kinds of double salts: in one the 2 eq. of fixed base are different protoxides, \bar{T} , $\left\{ \begin{smallmatrix} M O \\ m O \end{smallmatrix} \right.$; in the other, one of the equivalents of fixed base is replaced by 1 eq. of a sesquioxide, \bar{T} , $\left\{ \begin{smallmatrix} M O \\ m_2 O_3 \end{smallmatrix} \right.$. This latter kind may be considered basic, since the sesquioxide, $m_2 O_3$, usually neutralizes as much acid as 3 eq. of protoxide. Tartaric acid is remarkable for its tendency to form double salts.

Among the neutral tartrates are, the tartrate of ammonia, \bar{T} , 2 N H₄ O + 2 aq.; tartrate of potash, or soluble tartar, \bar{T} , 2 K O; tartrate of soda, \bar{T} , 2 Na O + 4 aq.; tartrate of lime, \bar{T} , 2 Ca O + 8 aq., &c. &c.

Among the acid salts are, acid tartrate of ethyle, or tartrovinic acid, \bar{T} , Ae O, H O — a crystallizable compound: acid tartrate of potash, or tartar, \bar{T} , K O, H O. This is the principal compound of tartaric acid. It exists in the juice of the grape, dissolved by the aid of the sugar present, and when that sugar is converted into alcohol, in which the tartar is insoluble, it is deposited on the sides of the fermenting casks. When purified it is quite white, and is called cream of tartar. It is much used in medicine as a safe and mild laxative. When calcined in a covered crucible it leaves a mixture of carbonate of potash and charcoal, called black flux. Hence carbonate of potash is called salt of tartar. Like all the tartrates, cream of tartar, when heated, gives off a very peculiar smell of burnt vegetable matter, peculiar to tartaric and racemic acids and their salts.

Among the very numerous double tartrates may be mentioned the tartrate of potash and ammonia, \bar{T} , K O, N H₄ O. The tartrate of potash and oxide of ethyle, \bar{T} , Ae O, K O. Tartrate of potash and boracic acid, \bar{T} , K O, B O₃; this is the soluble cream of tartar used as a laxative on the continent. Tartrate of potash and soda, \bar{T} , K O, Na O + 10 aq.; this is the salt of Seignette or Rochelle salt; it crystallizes in very large transparent prisms, and is used as a mild laxative. Tartrate of potash and peroxide of iron, \bar{T} , K O, Fe₂ O₃; this is the tartarized iron of the pharmacopœias. Tartrate of potash and antimony, \bar{T} , K O, Sb₂ O₃; this is tartar emetic, one of the most valuable remedies: it must be considered as a basic salt; for Sb₂ O₃, here substituted for H O or K O, in short for a protoxide, requires for its neutralization

an additional equivalent of tartaric acid. It then yields the compound $2\bar{T} + \begin{Bmatrix} \text{K O} \\ \text{Sb}_2\text{O}_3 \end{Bmatrix}$, which is neutral, since the bases contain 4 eq. of oxygen for 2 eq. of acid.

Tartar emetic is formed when 3 parts of oxide of antimony and 4 of cream of tartar are ground together, and made into a thin cream with water, which is heated to 158° , till a portion, tried separately, dissolves in 15 parts of cold water. When this is the case, 6 or 8 parts of water are added, and the whole boiled for half an hour. The liquid, filtered while hot, deposits, on cooling, crystals of tartar emetic. It forms white brilliant crystals which soon become opaque. It is soluble in 14 or 15 parts of cold water and 2 parts of boiling water. The crystals are \bar{T} , K O, Sb_2O_3 , + 2 aq.

When heated, the crystals first lose the 2 eq. of water of crystallization; and when the heat rises to 390° , 2 more eq. of water are given off, without the acid being destroyed. The salt is then $\text{C}_4\text{H}_4\text{O}_{10} + \begin{Bmatrix} \text{K O} \\ \text{Sb O} \end{Bmatrix}$. That is to say, 2 eq. of oxygen, from the oxide of antimony, have been expelled along with 2 of hydrogen from the acid. It has been already shown that tartar emetic, $\text{C}_4\text{H}_4\text{O}_{10} + \begin{Bmatrix} \text{K O} \\ \text{Sb}_2\text{O}_3 \end{Bmatrix}$, contains 2 eq. of oxygen in the bases, more than is required for a neutral salt; and it is apparently these 2 eq. of oxygen which are thus expelled as water. If we bear in mind that Sb_2O_3 is the equivalent of 3 K O, or, in other words, that $\text{Sb}\frac{2}{3}$ is equivalent to K or to H, we can then see that the tartar emetic heated to 390° is analogous in composition to neutral tartrate of potash.

Tartrate of potash is $\text{C}_4\text{H}_4\text{O}_{10} + \text{K}_2$

Tartar emetic, heated to 390° , is . . . $\text{C}_4\text{H}_4\text{O}_{10} + \begin{Bmatrix} \text{K} \\ \text{Sb}\frac{2}{3} \end{Bmatrix}$

In this point of view the 2 Sb are divided, $\frac{4}{3}$ Sb replacing hydrogen in the radical, and $\frac{2}{3}$ Sb replacing potassium in the base.

The neutral tartrate of potash and antimony, $2\bar{T}$, $\begin{Bmatrix} \text{K O} \\ \text{Sb}_2\text{O}_3 \end{Bmatrix}$ + 7 aq., is always formed in the mother liquors of tartar emetic. It is also formed when tartar emetic is dissolved in tartaric acid.

Tartar emetic forms a double salt with cream of tartar, \bar{T} , K O, Sb_2O_3 + 3 (\bar{T} , K O, H O). It crystallizes in scales.

The *Double Tartrate of Iron and Quinine*, (*Ferro-Tartrate of Quinine*), — Can be prepared by adding to a saturated solution of tartaric acid, pure quinine, and then moist hydrated sesquioxide of iron. The solution should be carefully evaporated to the consistence of syrup, poured on glass, and dried to brilliant red scales. This is a preferable preparation to the ferro-citrate of

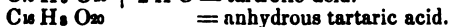
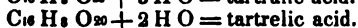
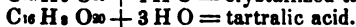
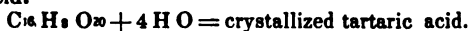
quinine, as it is more soluble in cold water. Its effect upon the system is the same as the double citrate. — (*Sanders*).

The *Ferro-Tartrate of Morphine* can be prepared as the above. The ferro-citrate and the ferro-tartrate of morphine, have proved valuable remedies in the hands of Professors Newton, King and Freeman. The *Ferro-tartrate of salicine* can be prepared as the above, substituting this alcooloid for quinine or morphine. — (*Sanders*).

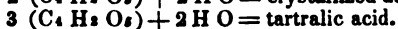
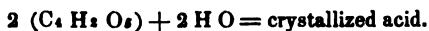
It is quite probable that double citrates and tartrates of quinine and morphine can be prepared with equal facility with the above. — (*Sanders*).

ACTION OF HEAT ON TARTARIC ACID.

When crystallized tartaric acid is heated, it melts, then loses $\frac{1}{2}$ of its water, leaving a new acid, tartralic acid; next it loses $\frac{1}{2}$ its water, and is converted into tartrelic acid; and finally it loses all its water and is converted into anhydrous tartaric acid. We may represent these changes as follows, doubling the formula of tartaric acid.



In tartralic and tartrelic acids, the neutralizing power is diminished, in so far that tartralic acid neutralizes $\frac{1}{2}$ less base, and tartrelic acid $\frac{1}{2}$ less base than tartaric acid. Both of these acids, as well as the anhydrous acid, are, by long boiling with water, reconverted into tartaric acid. It would appear as if in the tartralic and tartrelic acids, an additional quantity of anhydrous acid had been added to the radical without affecting the neutralizing power, just as in phosphoric, pyrophosphoric, and metaphosphoric acids. If we represent the anhydrous acid by $C_4H_4O_8$, then we have,



When tartaric acid, or rather anhydrous tartaric acid, is more strongly heated, it yields two pyrogenous acids, one liquid, the other crystallized. The former, $C_4H_2O_5$, H_2O , the latter $C_4H_2O_5$, H_2O . In fact, 2 eq. of anhydrous tartaric acid contain the elements of 1 eq. of each of these new acids, 5 eq. of carbonic acid, and 2 eq. of water. The liquid acid is called pyroracemic acid, being obtained also from racemic acid: the solid acid may be called pyrotartaric acid.

Tartralic acid, $C_4H_4O_8$, $2H_2O$, is obtained by cautiously heating tartaric acid, taking care not to cause it to become brown. It is combined with baryta, and the baryta separated from the soluble tartrate by diluted sulphuric acid. Tartralic acid forms a transparent mass, not crystalline, deliquescent, and soluble in

alcohol. It is converted into tartaric acid, slowly by cold water, rapidly by hot water. It appears to be bibasic, and most of its salts are soluble. By long contact with water, they are converted into tartrates and free tartaric acid.

Tartrelic acid, $C_{16}H_{12}O_{20}, 2H_2O$, is obtained by keeping the preceding acid long melted without raising the temperature. It is colored brown, is deliquescent, and dissolves both in water and alcohol. Water rapidly changes it into tartralic and tartaric acids. Its salts are soluble, and undergo the same change as those of tartralic acid.

Anhydrous tartaric acid, $C_4H_2O_5$, is prepared by rapidly heating $\frac{1}{2}$ oz. of tartaric acid in a porcelain capsule. It swells up very much, gives off water, and is at last converted into a porous white mass. This is now heated for some time, in an oil-bath, to a temperature of 302° , then powdered and well washed with cold water, and dried. It forms a white powder insoluble in water, alcohol, and ether. By the action of water and bases it is converted successively into tartrelic and tartaric acids. Pyroracemic acid, or liquid pyrotartaric acid, $C_6H_2O_8, HO = \overline{pR}, HO$, is one of the products of the distillation of tartaric and racemic acids. It is separated from the crystals which accompany it, combined with oxide of lead, and the well-washed pyrotartarate of lead decomposed by sulphuretted hydrogen. It is concentrated in vacuo, and forms a thick syrup nearly colorless, which cannot be distilled without partial decomposition. Its salts are not easily obtained in crystals, and when their solutions are heated, they lose the power of crystallizing. The general formula of the pyroracemates is $C_6H_2O_8, MO$. They are colored dark red by salts of protoxide of iron, and a crystal of sulphate of copper introduced into the solution of a pyroracemate causes a white precipitate. Pyroracemate of oxide of ethyle is a colorless liquid, of an aromatic smell, resembling that of acorus.

Pyrotartaric acid, $C_5H_2O_7, HO = p\overline{T}, HO$, is formed along with the preceding acid in small quantity by the distillation of tartaric acid; it is obtained far more abundantly by the distillation of cream of tartar. The product of the distillation, which is liquid, is evaporated till it crystallizes, and the mother liquid, acted on by nitric acid to destroy the oily impurities, and again evaporated, yields an additional quantity. The crystals melt at 230° , and volatilize at from 284° to 300° . The salts of this acid are soluble; that of lead appears to be rather sparingly so. But the results of different experimenters on this subject are so discordant that we must wait for farther researches.

3. RACEMIC ACID. $C_4H_2O_5, HO = \overline{R}, HO$? or $C_4H_2O_{10}, 2H_2O = R, 2H_2O$?

Syn. Paratartaric Acid.—This remarkable acid, which has the same composition in 100 parts as tartaric acid, and very similar

properties, is found along with tartaric acid in the grapes of certain districts. When both acids are present, the liquid obtained by boiling the tartrate and racemate of lime with diluted sulphuric acid, deposits, on evaporation, racemic acid in hard crystalline crusts, before tartaric acid, which is more soluble, begins to crystallize. It may be distinguished from tartaric acid by not forming a double salt of potash and soda.

The crystals of the racemic acid have a very sour taste, and are composed of $\bar{R}, H O + aq.$ At 212° they lose the 1 eq. of water of crystallization, and when more strongly heated, yield the same products as tartaric acid. The solution of racemic acid forms a precipitate of racemate of lime when mixed with chloride of calcium, which serves to distinguish it from tartaric acid; but like tartaric acid, it causes a crystalline precipitate in the salts of potash.

Racemic acid is possibly monobasic, and according to some, it does not, like tartaric acid, form double salts with two strong bases. It forms neutral salts, $\bar{R}, M O$, and acid salts, $\bar{R}, M O + \bar{R}, H O$. Thus the neutral racemate of potash is $\bar{R}, K O + 2 aq.$, and the acid racemate of potash, analogous to cream of tartar, is $\bar{R}, K O + \bar{R}, H O$. These two salts, therefore, have precisely the same composition as the corresponding tartrates. The acid racemate of potash, with oxide of antimony, yields a double salt analogous to tartar emetic, but of a different crystalline form. The relations of racemic acid to the oxides of ethyle and methyle are similar to those of tartaric acid. On the whole, racemic acid is interesting, from its presenting one of the best marked cases of isomerism, namely, with tartaric acid. In this case, not only is the composition the same, but the general properties, and most of the special ones, are identical. In fact, were it not that we must admit tartaric acid to be bibasic, we should find it difficult in any way to account for the differences which exist between the two acids. We have here, even on the supposition, which is doubtful, that racemic acid is monobasic, a very near approach to the occurrence of different properties with the same composition, and even the same arrangement. The two acid salts of potash, for example, are, on

this view, $C_4 H_4 O_8 \begin{cases} K O \\ H O \end{cases}$ for the bitartrate: and $C_4 H_2 O_8, K O + C_4 H_2 O_8, H O$ for the biracemate. If we represent the latter as follows: $C_4 H_2 O \begin{cases} K O \\ H O \end{cases}$, we see how very nearly alike they

are, even on the view we have adopted of the one acid being bibasic, and the other monobasic: and we must bear in mind that these two salts are strikingly similar in properties. The same remarks apply to the crystallized acids and to the double salts with antimony, although in the case of the two acids, we have evidence of one point of difference in the arrangement. Tartaric acid is

$C_4H_4O_6, 2H_2O$, while racemic acid is $C_4H_4O_6, H_2O + aq.$ and loses the water of crystallization at 212° .

Fresenius has recently investigated the racemates and has not been able to establish the true distinction between racemic and tartaric acids. More recently still, a double racemate of potash and soda has been obtained, which would lead us to admit racemic acid to be, like tartaric acid, bibasic. For the present, therefore, we cannot specify with certainty any difference of constitution between the two acids.

4. MALIC ACID. $C_4H_4O_6, 2H_2O = \bar{M}, 2H_2O$.

This acid is of very frequent occurrence in acid fruits, as in the apple, and especially in the unripe berries of *sorbus aucuparia*, or mountain ash. The best method of extracting it is to express the berries when they begin to turn red, and to add to the strained liquid a thin milk of lime so as not entirely to neutralize the acid. On heating, neutral malate of lime separates, and is removed by a skimmer. To the mother liquid more milk of lime is added cautiously, so as to produce an additional quantity of salt. The malate of lime is washed with cold water, and dissolved with the aid of heat in a mixture of 1 part nitric acid, and 10 of water. On cooling, acid malate of lime is deposited in regular crystals, which are almost always colorless. They are rendered quite pure by a solution in hot water and crystallization. From this salt, by the addition of acetate of lead, malate of lead is precipitated as a curdy white solid, which, if left in the liquid, changes into shining silky crystals. These, which are pure malate of lead, being decomposed by sulphuretted hydrogen, yield the acid, which when evaporated to a syrup, forms a granular crystalline mass, deliquescent in the air, of a strong but agreeable acid taste. When the crystallized acid is kept for some time at a heat of 280° , it melts, and the melted acid is gradually filled with crystals. Cold water removes the unchanged malic acid, which, if again heated, undergoes the same change, till at length all the malic acid is converted into these crystals, which are paramaleic or fumaric acid.

If malic acid be distilled by a sharp heat, a great part passes over in the form of a volatile crystallizable acid, the maleic acid. At a certain period of the distillation, if the retort be removed from the fire, the boiling residue having become turbid and thick, it suddenly becomes quite solid, and is found to consist of fumaric acid.

Malic acid is bibasic; in proof of which, it forms acid salts with lime, magnesia, and oxide of zinc, which monobasic acids never do. There are two series of malates: 1, Neutral, $\bar{M} 2 M O$; 2, Acid, $\bar{M}, M O, H O$. Most of the malates are soluble in water, but not in alcohol. Lime water, neutralized by malic acid, con-

tries clear whether cold or hot, which serves to distinguish it from tartaric, citric, racemic, and oxalic acids.

Acid malate of ammonia, $\bar{M}, NH_4 O, H O$, is best formed by neutralizing with ammonia one of two equal portions of malic acid (as prepared from the crude malate of lead by diluted sulphuric acid), and then adding the other portion, and evaporating to a syrup. On cooling, large and very regular crystals of the acid are deposited, which are easily decolorized by animal charcoal. This is an excellent method of purifying malic acid, when it is much contaminated with other substances. Acid malate of lime, $\bar{M}, Ca O, H O + 6 aq.$, is prepared as above described. It forms very regular and pure crystals, soluble in their own weight of boiling water, but requiring 20 parts of cold water. When malic acid is saturated with chalk, an acid liquid is obtained, which, when boiled, deposits the neutral malate of lime, $\bar{M}, 2 Ca O$. The malate of lead, $\bar{M}, 2 Pb O + 6 aq.$, is remarkable for changing when left in the liquid in which it has been formed, from a curdy white precipitate to a mass of fine silky needles. In hot water this salt melts into a mass like pitch in consistence. Acid malate of copper, $\bar{M}, Cu O, H O + 2 aq.$, forms splendid large crystals of a fine cobalt-blue color. There appears to be a basic malate of copper, $\bar{M}, 2 Cu O + Cu O + 6 aq.$, which forms green crystals. Malate of silver, $\bar{M}, 2 Ag O$, is a white powder, soluble in boiling water. The other malates are analogous to these, and possess little interest.

Maleic acid, $C_4 H_2 O_4 \cdot 2 H O = \bar{Ma}, 2 H O$, is prepared as above mentioned, by distilling malic acid. This acid is bibasic, but has the same composition, in 100 parts, as aconitic, or equisetio acid. It forms crystals, which are very soluble in water, alcohol, and ether. When heated sharply, it yields water, and a white volatile solid, melting at 134° , and boiling at 350° , which appears to be an anhydrous maleic acid. When the hydrated acid is kept melted for some time, it is changed, exactly as malic acid is, into fumaric acid. Hydrated maleic acid has precisely the same composition as anhydrous malic acid, which at once explains its formation.

The general formula of its salts is, $\bar{Ma} 2, M O$, for the neutral, and $\bar{Ma}, M O, H O$, for the acid maleates. It forms an acid maleate of silver, $\bar{Ma}, Ag O, H O$.

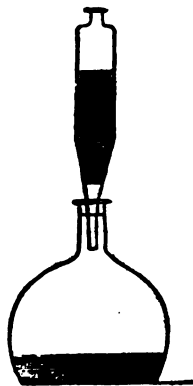
Fumaric or paramaleic acid, $C_4 H O_4, H O = \bar{Fu}, H O$, is formed, as above stated, by heating either malic or maleic acids to their melting point, and keeping them melted for a long time. It occurs in *fumaria officinalis*, and in Iceland moss. It forms saccharine scales requiring 200 parts of cold water for solution. It is soluble in alcohol.

It is a monobasic acid, but has the same composition in 100 parts as maleic acid, which at once explains its formation from malic, or from maleic acid. Its salts are sparingly soluble. The fumarate of oxide of ethyle is a heavy oily liquid, of an aromatic smell of fruits. When this ether, Fu, Ae O , is acted on by aqua ammoniac, it forms a white insoluble powder, which is fumaramide, $\text{C}_4\text{H}_2\text{O}_2 + \text{NH}_2$. This body has all the characters of a compound amide.

5. TANNIC ACID. $\text{C}_{12}\text{H}_8\text{O}_9, 3\text{H}_2\text{O} = \text{Qt}, 3\text{H}_2\text{O}$.

SYN. Quercitannic Acid. Tannine. — This acid occurs chiefly in oak bark and in nut-galls, an excrescence on oak-leaves, caused by the attacks of an insect, which apparently pierces the leaf in order to deposit its eggs.

To obtain it, coarsely-powdered nut-galls are acted on, in an apparatus of displacement by ether, free from alcohol, but saturated with water. When the ether, after being left some time, in contact with the powder, is allowed to drop into the lower vessel, it separates into two strata of liquid, the lower of which is a pure solution of tannic acid in water, which is drawn off and dried up after being washed with ether. The dry mass is redissolved in water, and again dried up in vacuo.



Tannic acid thus obtained is nearly white, and not at all crystalline. It is very soluble in water and has a most astringent taste without bitterness. It is soluble in weak alcohol, but hardly soluble in ether. The aqueous solution, if exposed to the air, absorbs oxygen, produces an equal volume of carbonic acid, and is converted into gallic and ellagic acids. The addition of the mineral acids to a solution of tannic acid, causes a precipitate, which is composed of tannic acid and the acid employed, (sulphuric, &c.,) and which is very soluble in pure water. The precipitate formed by sulphuric acid in a hot solution, dissolves in hot diluted sulphuric acid, and when this solution has been boiled a short time, it contains no tannic acid, the whole being converted into gallic acid.

Tannic acid combines with animal gelatine, forming an insoluble curdy precipitate. A piece of prepared skin, introduced into a solution of tannic acid, absorbs the acid, and is converted into leather. When heated, tannic acid is converted into metagallic and pyrogallic acids.

Tannic acid and its salts strike a deep blue, nearly black color with persalts of iron; and it likewise causes a precipitate in the solutions of most of the vegetable bases.

It is a tribasic acid, and the general formula for the neutral tannates is \overline{Qt} , 3 M O, in the case of protoxides, and 3 \overline{Qt} , $M_2 O_3$, in the case of sesquioxides. These salts, however, have been but little studied.*

The conversion of tannic acid into gallic acid is not fully understood. In some circumstances, it appears to depend on the absorption of oxygen; and in fact, 1 eq. tannic acid, plus 8 eq. oxygen, contains the elements of 2 eq. gallic acid, 4 eq. carbonic acid, and 2 eq. water. But when the conversion is produced by sulphuric acid, no other substance is formed with the gallic acid, except a coloring matter, which appears not to be essential. There is some probability that gallic acid exists ready formed in tannic acid; and if we subtract 2 eq. anhydrous gallic acid, 2 ($C_7 H_2 O_4$), from 1 eq. of hydrated tannic acid, $C_{12} H_2 O_{11}$, there is left $C_4 H_4 O_4$, which is the composition of hydrated acetic acid; or, tripled, that of dry grape sugar. As tannic acid, or at least the powder of nut-galls, if moistened, is said to be susceptible of the vinous fermentation, it is not impossible that tannic acid may contain gallic acid, plus sugar, if not gallic acid, plus acetic acid. Tannic acid is converted into gallic acid as rapidly by the action of an excess of alkali as by that of acid; but the whole subject requires investigation.

6. GALLIC ACID. $C_7 H O_3, 2 H O = \overline{G}, 2 H O$.

This acid exists in the seeds of mango, and is formed as above described by the decomposition of tannic acid. It is purified from coloring matter, by combining it with oxide of lead, and decomposing the gallate of lead, suspended in water, by sulphuretted hydrogen; the sulphide of lead acts as a decolorizing agent.

Pure gallic acid forms beautiful prisms of a silky lustre, and a slight yellowish color, of the formula $C_7 H O_3, 2 H O + aq$. It is sparingly soluble in cold water, requiring 100 parts, but dissolves in 3 parts of boiling water. Solutions of the acid and its salts, strike a black color with persalts and protopersalts of iron. When exposed to the air, the solution of gallic acid absorbs oxygen, and becomes dark-colored; this change is very rapid in the presence of alkalies, so that the alkaline gallates, especially if the alkali be in excess, are rapidly decomposed, and become nearly black.

When dissolved in hot oil of vitriol, and precipitated from the cold solution by water, gallic acid is obtained in a peculiar form,

* The tannate of the sesquioxide of iron is a deep black salt, soluble in water. It is the basis of common writing ink, which is, according to Sullivan, the tanno-gallate of iron. By properly boiling a solution of tannic acid and quinine, and when it is clear, adding carefully the moist hydrated peroxide of iron, a double salt, the *ferro-tannate of quinine*, is formed. It is a dark salt, but is not so elegant a preparation as the ferro-citrate and ferro-tartrate of quinine, (which see under the heads of these acids.)

as $C_7 H_2 O_4$, perhaps $C_7 H O_3 + H O$, in which the crystals have lost 2 eq. of water, 1 basic or hydratic, the other, water of crystallization. This peculiar gallic acid is a reddish-brown crystalline powder, which might be used in dyeing, as it yields colors on cloth, like those from madder. When heated it forms fine red prisms, which call to mind alizarine, the crystalline matter found in madder.

By the action of heat, crystallized gallic acid yields, like tannic acid, pyrogallic and metagallic acids.

The gallates are little known. They are very easily decomposed by the action of the air. The acid gallate of ammonia is $\bar{G}, N H_4 O + \bar{G}, 2 H O$. Acid gallate of lead has a similar composition. There is a bibasic gallate of lead, $\bar{G}, 2 Pb O$.

The recent investigations of Büchner, Junior, have shown that both the tannates and gallates are, in some respects anomalous, and require farther study.

When tannic, or gallic acid is heated by a sharp fire, carbonic acid, water and pyrogallic acid distil over, while a dark solid remains in the retort, which is metagallic acid.

Pyrogallic acid, $C_2 H O ? C_6 H_2 O_2 ?$ or $C_6 H_4 O_4 ?$ forms shining scales of a bitter and astringent taste; fusible at 240° , volatile at 410° . It is converted, by a stronger heat, into metagallic acid. It is formed from gallic acid, $C_7 H_2 O_4$, by the loss of 1 eq. carbonic acid. If acid at all, it is a very feeble acid, and nothing is known of its salts.

Metagallic acid, $C_{12} H_2 O_2, H O ? C_6 H_2 O_2 ?$ is produced as above mentioned, from tannic, gallic, and pyrogallic acids. It is a black powder, insoluble in water, soluble in alkalies. Of its salts little is known. It differs from gallic acid, only by the elements of carbonic acid: $2 (C_7 H_2 O_4) = 2 C O_2 + C_{12} H_4 O_4$. From pyrogallic acid it only differs by the elements of water.

Tannic acid contains the elements of gallic and pyrogallic acids. $3 (C_{12} H_2 O_2) = 6 (C_6 H_2 O_2) + 2 (C_6 H_2 O_2)$; and since either gallic or pyrogallic acid may produce metagallic acid, it is obvious that there is a close connection among these four compounds. The precise nature of this connection future experiments must ascertain.

When an infusion of nut-galls has been so long exposed to the air, that all tannic acid has disappeared, the gallic acid is found mixed with an insoluble, or sparingly soluble powder, which is a new acid, ellagic acid. Its composition is $C_7 H_2 O_5$, and when dried at 240° , $C_7 H_2 O_4$; so that it is isomeric with gallic acid, and with the modified acid produced by the action of oil of vitriol. It has not been much studied, and we do not know its actual atomic weight. When heated, it yields greenish yellow vapors, which condense into crystals of the same color, insoluble in water, alcohol, or ether, soluble in sulphuric acid and in alkalies.

This acid is said to occur in the root of *tormentilla vulgaris*; and is also the chief constituent of bezoar stones, which are a species of animal concretion. According to Mercklein and Wöhler, the acid of bezoar stones is $C_{14}H_2O_7 \cdot H_2O$; which is equal to twice the formula of ellagic acid, minus 1 eq. of hydrogen, for $2(C_6H_7O_4) = C_{14}H_2O_8$. The acids, according to Mercklein and Wöhler, are identical, and their formula, $C_{14}H_2O_7 \cdot H_2O = C_{14}H_4O_8$, is probably correct.

Tannic acid and the substances derived from it, occur in a good many plants, besides those of the genus *quercus*; the infusions of all of which are recognized by their striking a bluish-black with persalts of iron. But the astringent taste and the property of tanning, or combining with animal gelatine, are found in many plants, such as cinchona, kino, catechu, pinus, &c. These are distinguished by giving, with persalts of iron, either a dark green or a gray color. It has not been proved that they contain tannic acid, but Geiger has shown that these different colors may occur even when the same tanning principle is present, and that the green is owing at all events frequently, to the presence of free acid, while the addition of chalk, in some cases, changes the green to the characteristic bluish-black, due to tannic acid. There are, however, some reasons for admitting more than one tanning, or astringent principle. The whole subject requires investigation.

Catechu. Mimotannic Acid.

When catechu, the dried extract of *mimosa catechu*, is acted on by cold water, it yields a soluble matter very similar to tannic acid, if not identical with it when pure. It is, however, contaminated by some compound which causes it to redden when exposed to air. It does not appear to yield the same products when heated that tannic acid does; but this is uncertain, and may be caused by the presence of impurities. Berzelius proposes to call this tannic acid, mimotannic acid, from *mimosa*, to distinguish it from the tannic acid of galls, which he calls quercitannic acid, from *quercus*.

The portion of catechu insoluble in cold water, contains a peculiar compound, called catechine or tanningenic acid. It is soluble in hot water, and when pure forms a white silky crystalline powder which is said to be composed of $C_{18}H_8O_8$. When heated it is said to be transformed into (mimo?) tannic acid. By the action of caustic potash it yields a black acid, japonic acid, $C_{18}H_8O_8$, H_2O ? Carbonate of potash converts it into a red acid, rubinic acid, $C_{18}H_8O_8$ (?) in the anhydrous state. The hydrated acid is said to have the same composition as japonic acid, possibly, therefore, $C_{18}H_8O_8$? But as the japonic acid, on the same authority, Svanberg, in combining with silver, forms a salt $C_{18}H_8O_7 \cdot AgO$, in which 2 eq. of the acid have lost 2 eq. of water, and

gained only 1 eq. oxide of silver, it is evident that our knowledge of these compounds is very imperfect.

7. MECONIC ACID. $C_{14}H_{11}O_{11}, 3H_2O = \overline{Me}, 3H_2O$.

A tribasic acid, found only in opium, the dried juice of *papaver somniferum*. To prepare it, the crude meconate of lime, obtained in the manufacture of muriate of morphia, is mixed with twenty parts of boiling water, and three parts of strong hydrochloric acid added to the mixture, which must be removed from the fire, and not boiled after the acid has been added. On cooling, acid meconate of lime is deposited in shining crystals, which are collected on a cloth filter, squeezed, and treated a second time with the same quantities of acid and hot water. The strained acid liquid contains a large, but variable proportion of sulphate of lime always present, sometimes even to the extent of $\frac{1}{4}$ or $\frac{3}{4}$, in the crude meconate of lime. Hence the advantage of using so much hydrochloric acid, which also renders the meconic acid less soluble. This time, the crystals are meconic acid, still much colored. They are collected and squeezed as before, and to make sure that all lime is removed, a third time dissolved in 20 parts of hot water and 2 of hydrochloric acid. The addition of the acid not only removes the last traces of lime, but causes the meconic acid to crystallize almost entirely out of the liquid, it being nearly insoluble in diluted acid. The crystals washed with a little cold water, and dried at the ordinary temperature, are now pure from every thing but coloring matter, and when heated to redness, leave no residue.

To get rid of the color, the crystals are now mixed with warm water, and caustic potash gradually added, so as nearly but not quite to neutralize the acid. As soon as the point of neutralization is reached, the reddish color changes to green, and so much potash must be added that any farther quantity would produce the green color. The whole is then heated in the water-bath, till all is dissolved, hot water being added, if necessary. (Were the potash now in excess, the whole acid would be decomposed into oxalic and carbonic acids.) On cooling, the meconate of potash, $\overline{Me} \begin{cases} 2K_2O \\ H_2O \end{cases}$, crystallizes, forming a semi-solid mass, which is to be squeezed out. The color is carried off, for the most part, in the mother liquor, which is very dark, and the squeezed salt, after a second, or if necessary, a third, solution in hot water, crystallization, and squeezing, is snow-white. This purified meconate of potash is then acted on by pure hydrochloric acid, exactly as recommended for the meconate of lime, and after the third operation, yields perfectly pure and white meconic acid in beautiful silvery scales, which, to remove any traces of the acid mother liquid, adhering to them, may be once more dissolved in the

smallest possible quantity of hot water, avoiding a heat of 212° , which decomposes the acid; the pure acid is deposited on cooling, as $\overline{\text{Me}}, 3 \text{H O} + 6 \text{ aq.}$

Meconic acid, when gently heated, loses 6 eq. of water of crystallization. It is soluble in water and in alcohol. When boiled, its solution becomes colored, producing comenic acid, carbonic acid, and a dark brown coloring matter. If boiled with hydrochloric acid, it is resolved into comenic acid and carbonic acid, without the production of coloring matter. When the dry acid is heated to 250° , the same change takes place. When heated with excess of aqua potassæ, meconic acid is entirely decomposed into oxalic acid, carbonic acid, and a dark coloring matter. Its distinguishing character is that of causing, in persalts of iron, a deep blood-red color, but no precipitate.

It forms three series of salts, like other tribasic acids. Thus, there are three meconates of potash: 1. Acid, $\overline{\text{Me}}, \begin{Bmatrix} \text{K O} \\ 2 \text{H O} \end{Bmatrix}$; 2. Neutral, above mentioned, $\overline{\text{Me}} \begin{Bmatrix} 2 \text{K O} \\ \text{H O} \end{Bmatrix} \text{ aq.}$ Both of these crystallize. 3. Tribasic $\overline{\text{Me}}, 3 \text{K O}$. This is yellow, and does not crystallize. There are also three meconates of soda; two of lime, acid and neutral or bibasic; and two of silver, bibasic, $\overline{\text{Me}}, 2 \text{Ag O}, \text{H O}$, and tribasic, $\overline{\text{Me}}, 3 \text{Ag O}$. The meconate of peroxide of iron is very soluble, of an intense blood-red color, but as it cannot be obtained pure or crystallized, its composition is still unknown.

8. COMENIC ACID. $\text{C}_{15} \text{H}_2 \text{O}_8, 2 \text{H O} = \overline{\text{Co}}, 2 \text{H O}$.

The acid is formed, as above described, from meconic acid, by the action of heat, or of heat and an acid combined. 1 eq. dried meconic acid, $\text{C}_{14} \text{H O}_{11} + 3 \text{H O} = \text{C}_{14} \text{H}_4 \text{O}_{14}$, yields 1 eq. comenic acid, $\text{C}_{15} \text{H}_2 \text{O}_8, 2 \text{H O}$, and 2 eq. carbonic acid, 2C O_2 . The acid is readily obtained by boiling meconate of lime with an excess of diluted hydrochloric acid. It is deposited, on cooling, in colored crystals, which may be decolorized by recrystallization with the aid of animal charcoal. The pure acid has a slight yellow tinge, and is very sparingly soluble in cold water. When heated, it is resolved into carbonic acid, pyromeconic acid, and a small quantity of a third substance, paracomenic acid, which, in some few points, differs from comenic acid, but has the same composition, and in many points is so similar that it may possibly turn out to be essentially the same.

Comenic acid forms two series of salts, with 1 and 2 eq. of fixed base respectively. With persalts of iron it forms a deep red solution, which deposits black crystals of unknown composition.

Pyromeconic acid, $C_{10}H_2O_5, H_2O$, is obtained as a crystalline sublimate by heating meconic or comenic acids. In fact, 1 eq. comenic acid, $C_{12}H_4O_{10}$, contains the elements of 1 eq. pyromeconic acid, $C_{10}H_4O_8$, and 2 eq. carbonic acid, $2CO_2$. It forms very soluble four-sided prisms, rather styptic to the taste; the solution of which, forms, with persalts of iron, a crystalline salt of a fine red color, the powder of which is like vermilion. This salt is $Fe_2O_3 + 3C_{10}H_2O_5$. Pyromeconic acid is so feeble an acid, that we can hardly class it with acids. It has more analogy with such bodies as acetone, derived from acetic acid, as pyromeconic acid is from meconic or comenic acid. It has the same composition as pyromucic acid.

9. KINIC ACID. $C_7H_4O_4, 2H_2O$? or $C_{14}H_{11}O_{11}, H_2O$?

This very remarkable acid occurs in cinchona bark. It is obtained in the manufacture of sulphate of quinine, in the form of kinate of lime, from which the lime is easily separated by means of oxalic acid. The liquid filtered from the oxalate of lime yields, on evaporation, the kinic acid in crystals. The lime may also be removed by sulphuric acid, and any adhering sulphate of lime separated by alcohol.

The salts of kinic acid are somewhat anomalous. Thus there is a salt of lead, $C_7H_4O_4 \cdot 3PbO$, and a salt of copper, $C_7H_4O_4, CuO, H_2O$, while the crystals of kinic acid are $C_7H_4O_8$. All this would lead to the conclusion that the acid was a bibasic one, $C_7H_4O_4, 2H_2O$. But the kinate of lime and the kinate of silver, both quite neutral salts, are $C_{14}H_{11}O_{11}, CaO$, and $C_{14}H_{11}O_{11}, AgO$, as if the acid were monobasic, $C_{14}H_{11}O_{11}, H_2O = C_{14}H_{12}O_{12}$. If we assume the acid to be quadribasic, we can then bring all the above salts into one series.

Thus : Kinic acid would be	$C_{14}H_8O_8,$	$4H_2O$
Kinate of lead,	$C_{14}H_8O_8,$	$4PbO$
Kinate of copper,	$C_{14}H_8O_8,$	$\left\{ \begin{array}{l} 2CuO \\ 2H_2O \end{array} \right.$
Kinate of lime,	$C_{14}H_8O_8,$	$\left\{ \begin{array}{l} CaO + 10 aq. \\ 3H_2O \end{array} \right.$
Kinate of silver,	$C_{14}H_8O_8,$	$\left\{ \begin{array}{l} AgO \\ 3H_2O \end{array} \right.$

But the objection to this view is, that, if this be the true constitution of the acid, the salts of lime and silver ought to be very acid, instead of being quite neutral.

PRODUCTS OF THE DECOMPOSITION OF KINIC ACID.

When kinic acid or kinate of lime is distilled with diluted sulphuric acid and peroxide of manganese, there is obtained a new compound called kinone, as a sublimate of fine golden yellow crystals, soluble in water, and very volatile, having a pungent smell in the state of vapor. Their composition is $C_{25}H_8O_8$. When acted

on by reducing agents, it takes up 2 and 4 eq. of hydrogen, forming two new compounds, green and white hydrokinone. The green hydrokinone, $C_{25}H_{10}O_8$, is one of the most beautiful compounds known to chemists, forming long prisms, of the most brilliant gold-green metallic lustre, surpassing those of murexide in beauty. It is best formed by adding a few drops of sulphurous acid to a solution of kinone. When an excess of sulphurous acid is used, the white hydrokinone, $C_{25}H_{12}O_8$, is formed, which crystallizes in six-sided prisms. When acted on by oxidizing agents, the solution of white hydrokinone becomes dark red, nearly black, and almost immediately deposits the splendid crystals of the green compound. The latter is also formed, by simply mixing solutions of kinone and white hydrokinone, being intermediate between those bodies. Wohler, to whom we are indebted for most of our knowledge, in regard to these very curious compounds, has described a series of bodies obtained from the above by the action of hydrochloric acid, chlorine, and sulphuretted hydrogen. The following tabular view, contains the names and composition of these substances, as far as we yet know them.

Kinone,	C_{25}	H_8	O_8
Green hydrokinone,	C_{25}	H_{10}	O_8
White hydrokinone,	C_{25}	H_{12}	O_8
Chlorohydrokinone	C_{25}	$\left\{ \begin{array}{l} H_{10} \\ Cl_2 \end{array} \right.$	O_8
Chlorokinone,	C_{25}	$\left\{ \begin{array}{l} Cl_2 \\ H_8 \end{array} \right.$	O_8
Brown sulphohydrokinone,	C_{25}	H_{11}	$O_7 S_4$
Yellow ditto	C_{25}	H_{12}	$O_7 S_5$
Brown chlorosulphokinone,	C_{25}	$H_8 Cl$	$O_8 S_4 ?$
Orange ditto	C_{25}	$H_8 Cl$	$O_8 S_4 ?$

It will be observed that in all these formulæ the carbon remains unaltered, and that several are instances of pure substitution, as $C_{25}H_8O_8$, compared with $C_{25}\left\{ \begin{array}{l} H_8 \\ Cl_2 \end{array} \right. O_8$, and $C_{25}H_{12}O_8$, compared with $C_{25}\left\{ \begin{array}{l} H_{10} \\ Cl_2 \end{array} \right. O_8$. We can also see the relation of the sulphohydrokinones to kinone if we express them as follows: $C_{25}H_8\left\{ \begin{array}{l} O_7 \\ S \end{array} \right. + 3HS$; and $C_{25}H_{12}\left\{ \begin{array}{l} O_7 \\ S \end{array} \right. + 4HS$.

We come now to a class of acids of very distinct and peculiar characters; those, namely, which occur as the chief constituents of fat oils and fats, vegetable or animal. Of these oily acids there are two kinds: 1, those which are volatile and usually somewhat soluble in water; 2, those which have more the character of the oils and fats from which they are derived, and can seldom be distilled without decomposition. We shall begin with the volatile oily acids.

10. BUTYRIC ACID. $C_4H_7O_2, H_2O$.

This acid exists in small proportion in butter, in the form of a neutral butyrate of glycerine, or butyrine, to which the butter owes its peculiar and agreeable flavor. When butter is saponified by potash, and the solution of the soap is decomposed by tartaric acid, the oleic and margaric acids are separated as an oily stratum, while three or four volatile acids are dissolved in the water. These are butyric, caproic, capric, and caprylic acids. The butyric acid may be extracted from the mixture; but it is far better obtained by the fermentation of sugar. When sugar, either cane, grape, or milk sugar, is mixed with cheese, water, and chalk, and kept in a warm place, lactic acid is at first formed, which combines with the lime. But if the fermentation be continued at a pretty high temperature, 90° to 100° for example, the lactate of lime disappears, and is at last replaced by butyrate of lime, as explained under the head of butyric fermentation. This salt is now distilled with diluted hydrochloric acid, and the distilled liquid treated with chloride of calcium, when it divides into two strata. The lighter is butyric acid, still containing water. It is rectified until the boiling point rises to 318° . The previous portions contain water; what now passes is pure.

Bensch recommends to convert the butyrate of lime, by the addition of carbonate of soda, into butyrate of soda, and to mix the solution of this salt with sulphuric acid diluted with an equal weight of water, when the greater part of the crude butyric acid rises to the surface, and may be removed by a pipette. The acid solution of sulphate of soda, being distilled, yields an additional quantity of diluted butyric acid, which is saturated with soda, and the salt decomposed by sulphuric acid, which yields a second portion of crude butyric acid. The whole of the crude acid is now purified by rectification.

It is a clear, colorless, mobile liquid, of an odor resembling that of acetic acid and that of butter. An intense cold solidifies it. It is very acid and corrosive. Its Sp. G. is 0.963. It dissolves fats and fat oils.

Chlorine decomposes butyric acid, producing by substitution two acids, $C_4 \begin{Bmatrix} H_3 \\ Cl \end{Bmatrix} O_2, H_2O$; and $C_4 \begin{Bmatrix} H_2 \\ Cl_2 \end{Bmatrix} O_2, H_2O$. The latter crystallizes; and both form volatile fragrant compounds with oxide of ethyle.

Butyrate of lime is remarkable as being very soluble in cold water, but separating from the liquid in transparent prisms when it is boiled. Butyrate of baryta, when placed on the surface of water, exhibits the same motions as camphor. Butyrate of oxide of ethyle or butyric ether, $AcO, C_4H_7O_2$, is formed with singular facility by the mere mixture of alcohol and butyric acid with water and sulphuric acid. It rises to the surface as a very mobile

Liquid, of an odor somewhat similar to that of pine-apples. It is very soluble in alcohol. This ether is employed to flavor spirits: and there is reason to believe that the peculiar flavor of rum depends on the presence of a little butyric ether. Butyrate of oxide of methyle is quite analogous. Butyrate of oxide of glycercyle or butyrine exists in butter, and is supposed to be capable of being formed artificially, by warming a mixture of butyric, glycerine, and sulphuric acid. If the oil thus formed is really butyrine, it will be the first example of a compound of glycerine formed or reproduced artificially.

Butyramide, $C_4 H_7 O_2 + N H_3$, is formed when liquid ammonia acts on butyric ether: $Ac O, C_4 H_7 O_2 + N H_3 = Ac O, H O + C_4 H_7 O_2, N H_3$. It crystallizes in pearly scales.

Butyrone, $C_7 H_7 O$, analogous to acetone, is formed along with carbonate of lime, when butyrate of lime is distilled. $C_4 H_7 O_2, Ca O = C_7 H_7 O + Ca O, C O_2$. By the action of nitric acid, butyrone is converted into two new compounds; one, an ethereal fragrant liquid, lighter than water, the composition of which is not yet known: the other, an oily liquid, heavier than water, of an aromatic smell and a sweet taste, which is an acid, nitrobutyric or butyronitric acid. It is formed by substitution of $N O_4$ for H;

$C_7 \left\{ \begin{array}{l} H \\ N O_4 \end{array} \right. O, 2 H O$ from $C_7 H_7 O$. It forms crystallizable salts, and is bibasic, yielding two salts with oxide of silver, with 1 and 2 eq. of that oxide respectively.

By distillation with perchloride of phosphorus, butyrone is converted into an ethereal liquid, chlorobutyrene, the composition of which is $C_{14} H_{13} Cl$.

The caproic, capric and caprylic acids found in butter, are very analogous to butyric acid, but are not yet so well known. Caproic acid is $C_{12} H_{11} O_2, H O$. Its odor is like that of sweat. Caproate of oxide of ethyle has an odor somewhat analogous to that of butter. Capric acid is $C_{20} H_{19} O_2, H O$. It is very analogous to the preceding, but its odor is more like that of the goat. Caprylic acid is $C_{18} H_{17} O_2, H O$, and it is very analogous to the others.

It occasionally happens that butter, instead of yielding a mixture of volatile oily acids, of which butyric and caproic acid constitute the principal part, gives a mixture devoid of these acids, but containing in their place another acid, vaccinic acid, which is easily transformed into the other two. There can be no doubt that it contains the elements of butyric and caproic acids, $C_4 H_7 O_2, H O + C_{12} H_{11} O_2, H O = C_{16} H_{18} O_4$, or possibly $C_{20} H_{19} O_7 = C_{20} H_{19} O_6, H O$. In the latter case, it would require 1 eq. of water to yield the other acids. As, however, the solution remains neutral when vaccinic acid passes into caproic and butyric acids, it is most probably bibasic, $C_{20} H_{19} O_6, 2 H O$, and is, in fact, the sum of the other two. The cause of its occurrence is unknown.

Cenanthylic acid, $C_{14}H_{15}O_2$, $H O$, is formed by the action of nitric acid on castor oil, and has lately been detected by Redtenbacher among the products of the action of nitric acid on oleic acid, along with acetic, metacetic, butyric, valerianic, caproic, caprylic, pelargonic and capric acids, all belonging to the series represented as hydrates by $(CH)_n + O_4$, of which a table has been given at p. 259.

This acid, in composition, as well as in properties, is exactly intermediate between caproic and caprylic acids.

Cenanthole. — According to Bussy, when castor oil is distilled, there is formed a neutral oil, which he calls cenanthole, the formula of which is $C_{14}H_{15}O$, $H O$, and which bears to cenanthylic acid the same relation as aldehyde to acetic acid. It may also be viewed, doubling its formula, as a compound of cenanthylic acid with the oxide $C_{14}H_{15}O$, (analogous to oxide of ethyle), and in this view it corresponds to acetic ether, which is polymeric with aldehyde; thus, $2 C_{14}H_{15}O, H O = C_{14}H_{15}O + C_{14}H_{15}O_2$. Cetine (spermaceti) is an analogous compound, being either, as formerly explained, cetylate of oxide of setyle, $C_{32}H_{31}O + C_{32}H_{31}O_2$, or $C_{32}H_{31}O, H O$, analogous to aldehyde. In the cases of cenanthole and cetine, as only one compound is known, we cannot with certainty say whether the known compound corresponds to aldehyde or to acetic ether; but it is highly probable that in the case of all the acids of the series $(CH)_n + O_4$, both the compound analogous to aldehyde, and that analogous to acetic ether, are capable of existing. The following comparison will show the analogy:

Acids.	Aldehydes.	Ethers.
Acetic, $C_4H_5O_2, H O$;	$C_4H_5O, H O$;	$C_4H_5O, C_4H_5O_2$;
Cenanthylic, $C_{14}H_{15}O_2, H O$;	$C_{14}H_{15}O, H O$;	$C_{14}H_{15}O, C_{14}H_{15}O_2$;
	Cenanthole.	
Cetylic $C_{32}H_{31}O_2, H O$;	$C_{32}H_{31}O, H O$;	$C_{32}H_{31}O, C_{32}H_{31}O_2$;
		Cetine.

It will be observed, that the compounds in the second and third columns are, in each case, polymeric.

Pelargonic acid, $C_{15}H_{17}O_2, H O$. This acid, which belongs to the series above mentioned, and stands between caprylic and capric acids, is said to occur in the juice of *pelargonium roseum*, and was found, by Redtenbacher, among the products of the oxidation of oleic acid by nitric acid. It is little known.

Hircic acid is probably a mixture of capric and caprylic acids. Phocenic acid, found in small quantity in the oil of the dolphin, &c., has been found to be identical with valerianic acid.

Cevadic acid is a crystalline volatile acid, obtained from the seeds of *veratrum sabadilla*: composition unknown.

Veratric acid is contained in the same seeds. It is solid, crystallizable, and volatile. Its formula is $C_{10}H_8O_7, HO$. It forms a crystalline ether with oxide of ethyle; $AeO, C_{10}H_8O_7$.

Crotonic acid is another solid volatile acid, found in the seeds of *croton tiglium*. It has a pungent, acrid taste, and a nauseous smell. It forms crystallizable salts.

11. CAMPHORIC ACID. $C_{10}H_7O_3, HO = \overline{Ca}, HO$.

This acid is formed by the action of nitric acid on camphor. It forms crystalline scales, sparingly soluble in cold water, very soluble in alcohol and ether, fusible at 158° . These are the hydrated acid, which, if distilled, is resolved into water and anhydrous camphoric acid. The camphorates are not peculiarly interesting. With oxide of ethyle, camphoric acid forms two compounds: 1. Neutral, or camphoric ether, \overline{Ca}, AeO , an oily liquid, of a bitter taste and nauseous smell. 2. Acid, $2 \overline{Ca}, AeO, HO$, also called camphovinic acid, as it forms double salts, $2 \overline{Ca}, AeO, MO$. When chlorine acts on camphoric ether, Ca, C_4H_5O , it gives rise to the compound $Ca, C_4 \begin{cases} H_3O \\ Cl_2O \end{cases}$.

Anhydrous camphoric acid, $C_{10}H_7O_3$, forms, with bases, salts different from those formed by the hydrated acid. It is probable that it still retains some water replaceable by bases, being perhaps $C_{10}H_8O_3, HO$; or it may differ from ordinary camphoric acid as metaphosphoric acid does from common phosphoric acid. It is solid, crystalline, and volatile, and with dry ammonia forms a compound from which potash disengages no ammonia: with liquid ammonia it yields a salt different from camphorate of ammonia. Its action on oxide of ethyle has not been studied; but the subject deserves investigation.

By the action of sulphuric acid on anhydrous camphoric acid, there is formed, with disengagement of carbonic oxide, a new acid, sulphocamphoric acid $(C_9H_7O_3, SO_3)HO + 2aq$. This acid is crystallizable, and forms crystallizable salts of the formula $(C_9H_7O_3, SO_3)MO = C_9H_7SO_3, MO$.

CAMPHOR.

There are two kinds of camphor: that of Japan, or common camphor, $C_{10}H_{16}O$; and that of Borneo, $C_{10}H_{16}O$, or $C_{20}H_{32}O_2$. The properties of common camphor, and its peculiar smell, are well known. Its Sp. G. is 0.985 to 0.996; it is very volatile, evaporating at ordinary temperatures. Small fragments of camphor, on the surface of water, evaporate more rapidly, with rotatory movements. It dissolves in alcohol, and is precipitated by water. When distilled with anhydrous phosphoric acid, it yields a carbohydrogen, called camphogen, $C_{10}H_{14}$.

When camphor is passed in vapor over a heated mixture of hydrates of potash and lime, it yields a new acid, campholic acid, $C_{20}H_{17}O_2$, H_2O . Nitric acid, with the aid of heat, converts camphor into camphoric acid. The essence or oil of camphor of commerce is $C_{20}H_{16}O = 2$ eq. camphor minus 1 eq. oxygen.

Borneo camphor occurs in small crystalline fragments. Its odor is different from that of common camphor. I find that, if wrapped in paper, a distinctly alliaceous odor traverses the paper, and may thus be detected. Heated with phosphoric acid, it yields a carbo-hydrogen, $C_{20}H_{16}$; and this is also the composition of the essence which accompanies Borneo camphor. This essence is, therefore, Borneo camphor, $C_{20}H_{16}O_2$, minus 2 eq. water.

Common camphor is produced by the *laurus camphora*; Borneo camphor is the produce of *dryobalanops camphora*, and is, for some unknown reason, so highly prized by the Japanese, that it is not found in the markets of Europe.

Camphogen, $C_{20}H_{14}$, is the name given to the carbo-hydrogen obtained when common camphor is distilled with dry phosphoric acid. It occurs naturally in the oil of cummin. When acted on by sulphuric acid, it forms a new acid, sulphocamphic or hyposulphocamphic acid, $C_{20}H_{12}S_2O_5$, H_2O .

When camphor is passed over red-hot lime, another new compound is formed, namely, camphrone, $C_{20}H_{14}O = 3(C_{10}H_4O) - H_2 + O_2$. At a white heat camphor yields naphthaline, carburetted hydrogen, and carbonic oxide. 4 eq. camphor contain the elements ($C_{20}H_{12}O_4$) of 1 eq. naphthaline, $C_{20}H_8$; olefant gas, 2 C_4H_4 ; marsh gas, 8 CH_4 , and carbonic oxide, 4 CO .

12. VALERIANIC ACID. $C_{10}H_9O_2$, $H_2O = \overline{Va}$, H_2O .

This acid has already been mentioned as produced from hydrated oxide of amyle. It also occurs in the root of valerian. It forms two hydrates, \overline{Va} , H_2O , and \overline{Va} , $H_2O + 2$ aq.

The general formula of the valerates is \overline{Va} , $M O$. Valerate of oxide of ethyle, \overline{Va} , $Ac O$, is an oily liquid, of a smell like that of fruits and that of valerian at the same time.

By the action of chlorine, valerianic acid yields two new acids :

1. Chlorovalerisic acid, $C_{10} \left\{ \begin{matrix} H^6 \\ Cl_3 \end{matrix} \right. O_2$, H_2O .
 2. Chlorovalerosic acid, $C_{10} \left\{ \begin{matrix} H^5 \\ Cl_4 \end{matrix} \right. O_2$, H_2O .
- Both these compounds are formed by substitution without change of type.

When valerate of lime is distilled, it is said by Löwig to yield a volatile oily compound, valerone, $C_{10}H_8O = C_{10}H_8O_2 - CO_2$.

13. ANISEED ACID. $C_{16}H_8O_5$, H_2O .

This acid is obtained when the concrete essence of aniseed is acted on by nitric acid. It is crystallizable and volatile, and forms

salts which crystallize readily. When heated with an excess of baryta, it yields an oily liquid, called anisole.

The prolonged action of nitric acid on the concrete essence of anise produces another acid, nitro-anisic acid, in small yellow crystals. Its formula is $C_{10}H_7NO_5$, $H O = C_{10} \begin{Bmatrix} H_5 \\ NO_4 \end{Bmatrix} O_5, H O$. It is now found to be identical with nitrodraconic acid.

Anisole, the product formed when anisic acid is heated with baryta, is composed of $C_{10}H_7O_2 = C_{10}H_5O_2, H O - 2 C O_2$. It is formed, also, when the salicylate of oxide of methyle is heated with baryta. By the action of bromine, anisole gives rise to two new products, in which 1 and 2 eq. of hydrogen are respectively replaced by bromine; $C_{10} \begin{Bmatrix} H_5 \\ Br \end{Bmatrix} O_2$, and $C_{10} \begin{Bmatrix} H_5 \\ Br_2 \end{Bmatrix} O_2$. The latter is crystalline. Nitric acid acts violently on anisole, forming a crystalline mass, which dissolves in alcohol, with a rich green color, but is deposited in colorless needles, corresponding to one of the bromine compounds. Fuming sulphuric acid dissolves anisole, producing two compounds; one, insoluble in water, analogous to sulphobenzene: the other, soluble, an acid analogous to sulphovinic acid: $2 S O_3 + C_{10}H_7O_2, H O$.

Anisole, $C_{10}H_7O_2$, contains 1 eq. of hydrogen more than hyduret of benzoyl, $C_{10}H_5O_2, H$.

14. CENANTHIC ACID. $C_{14}H_{13}O_2, H O$.

This acid, in combination with oxide of ethyle, forming cenantthic ether, is found in wine, in the oil of grain spirit, and in some other fermented liquors. It is, as cenantthic ether, the cause of that peculiar odor of wine which adheres so remarkably to vessels in which wine has been kept, and enables us at once to say that an empty bottle or cask has contained wine. To obtain the acid, the ether is decomposed by caustic potash, and the cenantthate of potash distilled with dilute sulphuric acid. The hydrated acid is semisolid like butter, and is, in fact, a fat oil, insoluble in water, soluble in alcohol and ether.

Of its salts, the cenantthate of oxide of ethyle, cenantthic ether, is best known. It is a colorless liquid, of a peculiar vinous smell, which, when strong, has a stupifying effect. When hydrated cenantthic acid is distilled, it yields water, and anhydrous acid, more solid than the hydrate.

15. ROCCELLIC ACID. $C_{17}H_{15}O_2, H O ?$

This acid occurs in *rocella tinctoria*. It is crystallizable, insoluble in water, soluble in alcohol and ether. It has most of the properties of a fat acid, and its salts with the alkalies resemble soaps.

16. CUMINIC ACID. $C_{10}H_{11}O_2, H O$.

This acid is formed from the essential oil of cumin by oxidation with hydrated alkalies. It forms tabular crystals of singular

beauty. It is fusible and volatile, insoluble in cold water, soluble in alcohol and ether. When heated with caustic baryta, it yields a carbo-hydrogen, analagous to benzole, which is called cumene.

It forms well-defined salts with bases. Cuminat of oxide of ethyle, formed by passing hydrochloric acid gas through a solution of cuminic acid in alcohol, is an ethereal liquid, of a fragrant smell like that of apples.

Cumene, obtained by heating cuminic acid with bartya, is a colorless liquid, of a sweet smell. It is formed from cuminic acid; $C_{20}H_{12}O_4$, by the loss of 2 eq. carbonic acid, exactly as benzole is formed from benzoic acid; and its formula is consequently $C_{20}H_{12}$. Both nitric and sulphuric acid act on it and form new compounds, not yet fully examined. That formed by sulphuric acid is an acid, sulphocuminic acid, $C_{18}H_{11}, S_2O_5 + H.O$.

Essence of cumin (*cuminum cyminum*) contains two oils: 1. Cuminole, $C_{20}H_{12}O_2$, which is the true oil of cumin, analogous to hyduret of benzoyle; 2. Cymene, $C_{20}H_{14}$, isomeric with camphogen. It is an oil of an agreeable odor of lemons. The oil is acted on by nitric and sulphuric acids, which produce two new acids. That formed with sulphuric acid is $C_{20}H_{12} + S_2O_5, H.O$.

Cuminole, $C_{20}H_{12}O_2$, may be viewed as analogous to hyduret of benzoyle, in which case it becomes $C_{20}H_{11}O_2 + H$, the hyduret of a new radical, cumyle. Cuminic acid then becomes $C_{20}H_{11}O_2, O + H.O$, analogous to benzoic acid. Chlorine acts on hyduret of cumyle, producing a compound, $C_{20}H_{11}O_2, Cl$, which is chloride of cumyle. Adopting the symbol $Cm = C_{20}H_{11}O_2$, we have CmH , $CmO + H.O$, and $CmCl$, analogous to BzH , $BzO + H.O$, and $BzCl$.

17. EUGENIC ACID. $C_{20}H_{12}O_4$? or $C_{20}H_{12}O_5$?

This acid is found in cloves, along with a neutral oil, $C_{10}H_8$, or $C_{20}H_{16}$. The latter is separated by potash, and the eugenic acid obtained by distilling the salt of potash with dilute sulphuric acid. It is an oily liquid, of Sp. G. 1.079, having the strongest odor of cloves. It forms crystallizable salts with bases, and among them an acid salt of potash, $2 C_{20}H_{12}O_4 + KO + H.O$?

Cloves, likewise, contain two crystallizable compounds: 1. Caryophylline, which forms yellow prisms; of the formula $C_{20}H_{16}O_2$, an oxide, therefore, of the neutral oil of cloves. 2. Eugenine, which forms yellow pearly scales, the composition of which is the same as that of eugenic acid.

18. COCINIC ACID. $C_{28}H_{42}O_2, H.O$.

This acid, the first of the proper fat acids which we have come to, is found in the butter of the cocoa-nut combined with glycerine. The butter is saponified by potash, and the soap produced is decomposed by a mineral acid, when the fatty acid rises to the

surface. It is purified by being again saponified, and finally by crystallization in alcohol. It forms snow-white crystalline scales, fusible at 95° , and volatile. The salts of this acid with the alkalies are soaps like those of all fatty acids. Cocinate of oxide of ethyle is a colorless ether, with a very fragrant smell of apples. Cocinic acid belongs to the series $(\text{C H})_n + \text{O}_4$.

19. MYRISTIC ACID. $\text{C}_{22}\text{H}_{42}\text{O}_2, \text{H O}$.

This acid, which also belongs to the series $(\text{C H})_n + \text{O}_4$, is found combined with glycerine, as a fat or butter, in the berries of *myristica moschata* or nutmeg. There are two fats in the seeds, one red and unctuous, the other, myristine, white, and crystalline. It is easily purified by dissolving it in hot alcohol, in which it is, like the cocinate of glycerine, very soluble. On cooling, the pure myristine or myristate of glycerine is deposited as silky needles, which being saponified by potash, and the soap decomposed by an acid, yield myristic acid. The acid is purified by means of alcohol. It melts at 118° , and is decomposed by distillation.

The salts of this acid with the alkalies are soaps, very soluble in alcohol; and their aqueous solutions do not become viscid orropy when concentrated. Myristate of oxide of ethyle is a colorless oil. Myristate of oxide of glycercyle or myristine is purified as above described. It is a beautifully crystalline fat, melting at 88° . It is saponified with difficulty, and only by fusion with solid potash. It does not appear to contain ordinary glycerine: at least its formula would indicate a glycerine composed of $\text{C}_3\text{H}_2\text{O}$. This point is at present very obscure.

The formula of hydrated cœnanthic acid, doubled, or $\text{C}_{22}\text{H}_{42}\text{O}_2$, contains 2 eq. of oxygen more than 1 eq. of hydrated myristic acid, $\text{C}_{22}\text{H}_{42}\text{O}_4$; or the formula of dry cœnanthic acid doubled, $\text{C}_{22}\text{H}_{42}\text{O}_4$, contains 1 eq. of hydrogen less and 1 eq. of oxygen more than dry myristic acid, $\text{C}_{22}\text{H}_{42}\text{O}_2$.

20. PALMITIC ACID. $\text{C}_{26}\text{H}_{52}\text{O}_2, \text{H O}$.

This is the principal fat acid of palm oil. It is extracted by the usual process for fatty acids, and purified from oleic acid by crystallization in alcohol. It forms brilliant scales, similar to margaric acid, and melting at the same point, 140° , as that acid. It may be distilled in great part unchanged. Chlorine decomposes it, giving rise to new compounds.

The salts of this acid with the alkalies are soaps, and palm oil is much used in soap-making. Palmitate of glycerine, or palmitine, is the fat or butter of the palm oil, purified from the oleine or liquid part, by pressure, and then by crystallization in ether. It melts at 118° , and on cooling assumes the aspect of wax. Like myristine, it appears to contain the modified glycerine $\text{C}_3\text{H}_2\text{O}$, or oxide of lipyle, which is $\text{C}_3\text{H}_7\text{O}_2 - 3\text{H O}$;

that is, glycerine, minus 3 eq. of water, and divided by 2. Pure palmitine (as also pure myristine), when distilled, yields acroleine, derived from the glycerine; but no sebatic acids. The crude palm oil, or impure palmitine, however, yield abundance of sebatic acid, a compound derived from oleic acids, and proving, therefore, the presence of oleic acid or rather oleine.

21. CETYLIC ACID. $C_{26}H_{52}O_2, H_2O$.

SYN. *Ethalic Acid*. — This acid, which is isomeric with the preceding, is formed when ethal (hydrated oxide of cetyl) is heated with hydrates of lime and potash, or when cetine (spermaceti, cetylate of oxide of cetyl) is fused with potash, and the cetylate of potash decomposed by a stronger acid. It belongs of course, with the preceding acid, to the series $(CH)_n + O_2$. It is separated as usual in the case of fatty acids. It is a solid, fusible between 130° and 140° , and at 131° solidifying in radiated groups of needles. It may be distilled unaltered. Its salts are like those of the preceding acids.

22. MARGARIC ACID. $C_{24}H_{48}O_2, H_2O$; or, $C_{24}H_{46}O_2, 2H_2O$.

This is one of the most abundant and important of the fatty acids. Combined with glycerine, or margarine, it occurs in human fat and some other animal fats, and in many vegetable fats, such as olive oil. The acid may be extracted from soap made of these fats, but as it is mixed with much oleic acid, it is better to prepare it by oxidizing stearic acid (see below) by nitric acid, or by distilling either tallow or crude stearic acid. In the latter case, the product is well squeezed and purified by solution in alcohol, and crystallization. If prepared from pure stearic acid by nitric acid, it is pure from the first. It belongs to the series $(CH)_n + O_2$, and it is probably in consequence of its composition, that, like the other acids of that series, it is volatile without decomposition.

Margaric acid is a white solid fat, of distinct acid properties, fusible at 140° , very soluble in hot alcohol and in ether. It instantly combines with bases, decomposing the carbonates and forming perfect soaps with potash and soda. The neutral margarates of potash and soda are decomposed by the addition of much water, depositing the acid margarates in pearly scales. Margarate of glycerine, or margarine, is found pure in the solid part of human fat or of olive oil. It dissolves in hot alcohol, and crystallizes on cooling. Margarate of oxide of ethyle is a white fusible solid.

The general formula of the neutral margarates is $C_{24}H_{48}O_2, M_2O$, or $C_{24}H_{46}O_2, 2MO$. We cannot say with certainty whether margaric acid is unibasic, as the first of these formulæ would indicate, or bibasic, according to the second. We shall return to this point after describing stearic acid, and we shall also then describe the action of heat on both acids.

23. STEARIC ACID. $C_{18}H_{36}O_2, 2H_2O = \overline{St}, 2H_2O$.

This is, perhaps, the most important and most abundant of the fatty acids. It exists, in combination with glycerine, as stearine in beef and mutton fat, and in several vegetable fats, such as the butter of cacao. To obtain it, mutton suet is saponified by boiling with potash, and the purified soap decomposed by an acid, when a mixture of stearic and oleic acids, the latter in small proportion, rises to the surface. It is strongly pressed between warm plates, so as to get rid of the oleic acid in great part, and it is finally purified by solution in hot alcohol, and crystallization, repeated till its melting point is constant at 167° . Or the stearic acid of commerce, which is nearly pure, may be purified by means of alcohol. Or again, tallow may be mixed with half its weight of oil of vitriol, and the mass melted in hot water, which removes a compound of sulphuric acid with glycerine, while the stearic acid rises to the surface, and is to be purified as above. Finally, pure stearine, if saponified, and the soap acted on by an acid, yields at once pure stearic acid.

Stearic acid is a white solid, fusible at 167° , and on cooling, forming brilliant white needles. It may be reduced to powder, and is, like all fat acids, insoluble in water, soluble in alcohol and ether. It burns like wax, and is used in the formation of improved candles.

By the action of nitric acid and other oxidizing agents, stearic acid is at once converted into margaric acid, and it will be seen that the addition of 1 eq. oxygen is sufficient to effect this change. $C_{18}H_{36}O_2, 2H_2O + O = C_{18}H_{34}O_2, 2H_2O$.

Stearic acid is bibasic, and forms two series of salts; $St\ 2M\ O$, and St, MO, HO . The neutral stearates of the alkalies are perfect soaps. They dissolve in from 10 to 20 parts of hot water, and the addition of a large quantity of water decomposes them into acid stearates which are deposited, and basic stearates which remain dissolved. For the same reason, a hot solution of a neutral stearate becomes gelatinous on cooling, from the separation of the acid salt. Acid stearate of oxide of ethyle, $St, Ae\ O\ H\ O$, and neutral stearate of the same base, $St, 2\ Ae\ O$, are both white crystalline fusible solids; as is likewise the stearate of oxyde of methyle, $St, 2\ Mt\ O$.

Stearine, the chief ingredient of suet and tallow, appears to be the acid stearate of oxide of glycerile, but its precise formula cannot be determined as long as we are doubtful about that of glycerine. If glycerine be C_3H_5O , then stearine will be $C_{18}H_{36}O_2 + C_3H_5O + 2H_2O = \overline{St}, Gly\ O, 2H_2O$: but if stearine be $C_{18}H_{34}O_2$, the formula will be $2(C_{18}H_{34}O_2) + Gly\ O + 2H_2O$, (using the older formula for stearic acid.) Neither of these formulæ is satisfactory, as both exhibit three eq. of base and basic water, instead of two or four. When boiled with alkalies, stearine, like all other fats, is saponified: that is, the stearic acid combines with the

alkali, forming soap, and glycerine is separated. Pure stearine is obtained by pressing tallow between hot plates, and afterward dissolving in hot ether, which on cooling deposits the stearine. It is like wax when it has been melted, and it may be powdered.

Stearate of lead is an insoluble fusible soap, or, as it is called, a plaster. The same is true of margarate of lead, and in general of the compounds of lead with fat acids.

The composition of stearic acid stands in a very simple relation to that of margaric acid. If we call the compound $C_{24}H_{48}$, margaryle, and view it as a compound radical, representing it by the symbol Ml , then $MlO_2 =$ stearic acid, and $Ml_2O_2 = 2MlO_2 =$ margaric acid. These acids, therefore, bear to each other the same relation as that which subsists between sulphuric and hyposulphuric acids, SO_2 and S_2O_2 . The only difference is, that while SO_2 neutralizes as much base as S_2O_2 , MlO_2 only neutralizes half the quantity of base neutralized by Ml_2O_2 , or in other words, Ml_2O_2 neutralizes as much base as Ml_2O_2 .

When stearic acid is distilled alone, or with lime, it yields much margaric acid, and a neutral fusible crystalline fat, margarone, besides a solid carbo-hydrogen $C_{24}H_{48}$, carbonic acid and water. Margarone is either $C_{23}H_{46}O$, or $C_{24}H_{48}O$. In the former case, it is formed from margaric acid by the loss of 1 eq. carbonic acid; in the latter, it is the oxide of the supposed radical margaryle, MlO . The production of these compounds is easily understood, for 2 eq. stearic acid are equal to 3 eq. margaric acid, and 1 eq. oxide of margaryle: $2Ml_2O_2 = 3MlO_2 + MlO$. Again, 4 eq. of hydrated stearic acid contains the elements of 6 eq. hydrated margaric acid, 1 eq. margarone, ($C_{23}H_{46}O$), 1 eq. water, 1 eq. carbonic acid, and 1 eq. of the carbo-hydrogen $C_{24}H_{48}$. It would appear that according to circumstances, the margarone has a different composition, its properties varying little, so that different chemists have obtained different margarones: namely, $C_{23}H_{46}O$; $C_{24}H_{48}O$; and even $C_{24}H_{48}O = Ml_2O$. When margaric acid is heated, part distills unchanged, and part is converted into the above products.

When margarine or stearine are distilled, they yield the very acrid vapors of acroleine, a product derived from the glycerine contained in these fats; but pure stearic and margaric acids yield not a trace of acroleine. Neither do they yield any sebatic acid among the products of their distillation, this acid being derived exclusively from oleic acid.*

* The late investigations of MM. *Laurent* and *Gerhardt* have resulted in proving the atomic weights of margaric and stearic acids the same. They were led to these investigations from the strong resemblances which these acids bear to each other in their physical properties, and their metamorphoses under various re-agents. Stearic and margaric acids now bear the same relation to each other, that tartaric and racemic acids do; for while the latter are tar-

ACTION OF NITRIC ACID ON MARGARIC ACID.

By the action of nitric acid, stearic acid is converted into margaric acid, with disengagement of nitrous acid vapors. But if the action of the nitric acid be prolonged, the margaric acid is gradually oxidized and dissolved, being converted into suberic acid, succinic acid, and an oil soluble in nitric acid.

24. SUBERIC ACID. $C_8H_6O_3, HO = \bar{S}u, HO$.

This acid is formed, when cork is oxidized by nitric acid, but especially when nitric acid acts on stearic acid, margaric acid, oleic acid and other fatty bodies. The acid solution obtained by boiling stearic or margaric acid with nitric acid, till it is entirely dissolved, is evaporated to one half, and on cooling, deposits a large quantity of suberic acid, which is easily purified by crystallization.

It forms small granular crystals, fusible, when moist, at 130° , when dried, at 248° , volatile at a higher temperature, and subliming in the form of long needles. It is sparingly soluble in cold water, very soluble in hot water, in alcohol and ether.

The general formula of the suberates is Su, MO . The suberate of oxide of ethyle, is prepared like the ethers of all the fatty acids by passing hydrochloric acid gas through the alcoholic solution of the acid. When suberate of lime is distilled, it yields, among other oily products, a liquid boiling at 366° , the formula of which is, C_8H_7O . It may be either the oxide of C_8H_7 , or the hyduret of C_8H_6O . It is converted into suberic acid by the action of the air and of nitric acid. In fact, the addition of 3 eq. of oxygen gives the composition of hydrated suberic acid, $C_8H_7O_4$. It is probable that there exists a radical suberyle $= C_8H_6O = Su$; and that we have SuH , and SuO_2, HO , for the oil and suberic acid, analogous to the hyduret of benzoyle and benzoic acid.

25. SUCCINIC ACID. $C_4H_2O_3, HO = \bar{S}, HO$.

This acid exists ready formed in amber, and may be obtained by distilling that body. But the mother liquor of the suberic acid, formed from margaric acid, &c., by nitric acid, contains a large quantity of succinic acid, along with a little suberic acid. The mixture being dried up, is acted on by ether, which dissolves the suberic acid, leaving the succinic acid; it is finally purified by sublimation.

It forms regular crystals, which may be easily sublimed. The formula of the sublimed crystals is $2(C_4H_2O_3) + HO$; but by

taric and metataric acids, the others are stearic and metastearic acids. These investigations do away with the non-identity of the fat of the human species and that of other animals. These results must be of the highest importance to physiology.

repeated sublimation it may be obtained anhydrous. The first hydrate, \bar{S} , H_2O , melts at 356° , and boils at 455° , subliming, however, slowly at 284° . The sublimed hydrate, $2Su + H_2O$, melts at 320° , and boils at 468° ; and the anhydrous acid melts at 257° , and boils at 482° .

By the action of anhydrous sulphuric acid, it yields a new acid, apparently $C_8H_7S_2O_{10}$, $4H_2O$, hyposulphosuccinic acid.

The constitution of the succinates is still doubtful; but the most recent researches of Fehling, who has twice examined these salts with care, lead to the general formulæ of $C_4H_5O_3$, MO , for the neutral, and $2(C_4H_5O_3) + MO, H_2O$, for the acid salts. The succinates of lead present some anomalies. By the action of ammonia, NH_3 , on succinic ether, $C_4H_5O_3$, C_4H_5O , there is formed succinamide, $C_4H_5O_2, NH_2$, while alcohol, C_4H_5O, H_2O , is given off. When acid succinate of ammonia is heated, there is sublimed a new body, bisuccinamide, $C_8H_7O_4, NH_2$. It is formed from 2 eq. succinic acid and 1 eq. ammonia, by the separation of 2 eq. water. In their mode of formation these two bodies resemble oxamide and oxamic acid, only bisuccinamide has no acid properties.

The origin of amber is very uncertain; but it is most probably derived from some resin, formerly liquid or soft. It may possibly have arisen from the slow oxidation of a fatty matter, as we see succinic acid formed from fats by oxidation. Amber is a clear brittle yellow solid, becoming electric by friction. It is for the most part, insoluble in all menstrua. When heated it yields succinic acid and a volatile oil, and there is left a large proportion of a matter which may be called bituminous, and forms the principal part of the amber.

26. OLEIC ACID. $C_{18}H_{33}O_2, HO = \bar{O}$, H_2O .

This acid, in combination with glycerine, constitutes, as oleine, the liquid or most fusible portion of fats and fat oils. It exists in small proportion in tallow or suet; more abundantly in human fat, hog's lard, and butter; and it predominates in olive oil, and especially in almond oil. To obtain it, almond oil is saponified, and the mixed fat acid obtained from the soap is digested with half its weight of oxide of lead, by which means margarate and acid oleate of lead are formed. Ether dissolves the latter only, and the ethereal solution of oleate of lead is acted on by hydrochloric acid when the ether rises to the surface, holding the oleic acid in solution. The ether being distilled off, the oleic acid is left somewhat colored, and it is purified by exposure to cold, when the pure acid crystallizes; or by converting it into oleate of baryta, which is purified by means of alcohol. When pure it is a nearly colorless oily fluid, freezing in cold weather. At temperatures above 57° it is a fluid oil, but when once melted, it does not solidify till cooled

to 40° , and when solid it does not melt till heated to 57° . It rapidly absorbs oxygen from the air, and becomes brown.

It forms salts with bases, and the oleates of the alcalies are soaps. Naples soap is chiefly oleate of potash : oleate of soda is harder.

Nitric acid converts oleic acid into suberic acid and other products. By hyponitric (nitrous) acid or nitrate of mercury it is converted into elaidic acid.

When distilled, oleic acid gives rise to sebacic acid, and this is an infallible test of the presence of oleic acid or oleine in any fat. This character applies to all the varieties of oleic acid, although we have reason to think that the oleic acids of fat oils and of drying oils are very different. Indeed, according to recent researches, the oleic acid of linseed oil is $C_{18}H_{32}O_2$, $H O$.

Of the oleates, the most important are those of potash and soda, which exist in most soaps, and constitute the chief part of those made with olive or almond oil, or whale oil, and that of lead, which is a valuable ingredient of most plasters. Oleate of oxide of glycerile, as already mentioned, is oleine, the liquid part of fats and fat oils, which is hardly known in a perfectly pure state. Oleate of oxide of ethyle is an oily liquid.

27. SEBACIC ACID. $C_{10}H_{18}O_2$, $H O = \overline{Se}$, $H O$.

When any oil or fat, containing oleine or oleic acid, is distilled, and the product boiled with water, the hot filtered liquid deposits, on cooling, sebacic acid in small crystals resembling benzoic acid. It is soluble in alcohol and ether, and sublimes without alteration. The salts of sebacic acid are not remarkable, with the exception of the sebate of oxide of ethyle, which has a fragrant smell of melons. When we wish to ascertain the presence of oleine in a fat, a portion is distilled, the product is boiled with water, and the liquid, even if it deposit nothing, is tried by acetate of lead, with which it forms a white precipitate if sebacic acid be present.

28. ELAIDIC ACID. $C_{18}H_{32}O_2$, $H O$.

This acid is formed by the action of nitrous acid on oleic acid, with which it is isomeric. If a current of nitrous acid be passed through well-cooled oleic acid, the latter soon solidifies in large scales, which are elaidic acid. It is purified by solution in alcohol. It forms silvery scales, melting at 112° , very soluble in alcohol, and volatile without decomposition, except to a very small extent. The salts of this acid are soaps, and resemble those of the other fat acids.

Oleine is converted into elaidine (elaidate of glycerine), and oleic ether into elaidic ether, by the action of nitrous acid ; but we cannot yet account for the production of elaidic acid in these

cases or in that of its formation from oleic acid, since the mode of action of the nitrous acid is quite obscure.

ACTION OF NITRIC ACID ON OLEIC ACID.

When oleic acid is acted on by nitric acid, it yields several acids, only one of which, suberic acid, occurs in the action of nitric acid on other fat acids. The remaining acids are, azelaic acid? pimelic acid, adipic acid, lipic acid, and azoelic acid, all of which are crystallizable, besides no less than nine volatile acids, all belonging to the series $(CH)_n + O_4$. — (*Redtenbacher*).

The action of nitric acid on oleic acid is violent. When completed, the liquid is evaporated to one-half, and on cooling deposits suberic acid, which, according to Laurent, is accompanied by azelaic acid, very similar to it, the composition of which he describes as the same as that of suberic acid, or only differing by 1 eq. of water, while he gives the formula $C_{10}H_8O_4, H_2O$, that of suberic acid being $C_8H_6O_3, H_2O$. There is probably here an error of the press. But the existence of azelaic acid is very doubtful.

Pimelic acid crystallizes on evaporation after the suberic acid has been removed, in hard granular crystals, fusible and volatile. Its formula is $C_7H_5O_3, H_2O$. In the mother liquid are found: Adipic acid in round radiated masses, fusible and volatile: formula $C_6H_4O_3, H_2O$ (*Laurent*), $C_6H_5O_7, 2H_2O$ (*Bromeis*), probably different acids. The Lipic acid forms long tables, very fine when formed in alcohol: formula $C_5H_3O_4, H_2O$. Azoelic acid, according to Laurent, occurs in the form of an oily liquid, and œnanthis acid is also found. According to Bromeis, azoelic acid is doubtful, and the acid taken for it and for œnanthis acid is impure butyric acid, one of the oily acids observed in this reaction by Redtenbacher.

The volatile oily acids detected by that chemist are the following, being the first nine in the series so often mentioned, in which the hydrated acids have the formula $(CH)_n + O_4$. We give them in a tabular form, with the empirical and rational formulæ:

Acetic acid . . .	$C_4H_4O_4 = C_4H_5O_3, H_2O$.
Metacetic acid .	$C_6H_6O_4 = C_6H_5O_3, H_2O$.
Butyric acid . . .	$C_8H_8O_4 = C_8H_7O_3, H_2O$.
Valerianic acid .	$C_{10}H_{10}O_4 = C_{10}H_9O_3, H_2O$.
Caproic acid . . .	$C_{12}H_{12}O_4 = C_{12}H_{11}O_3, H_2O$.
œnanthyl acid .	$C_{14}H_{14}O_4 = C_{14}H_{13}O_3, H_2O$.
Caprylic acid . .	$C_{16}H_{16}O_4 = C_{16}H_{15}O_3, H_2O$.
Pelargonic acid .	$C_{18}H_{18}O_4 = C_{18}H_{17}O_3, H_2O$.
Capric acid . . .	$C_{20}H_{20}O_4 = C_{20}H_{19}O_3, H_2O$.

In this remarkable series of acids, each individual differs from the preceding by the addition of C_2H_2 ; and in like manner, the boiling point of each rises an equal number of degrees above

that of the preceding one. The three or four highest in the series are even solid at ordinary temperatures, and it is probable that in all the melting point rises with the amount of $C_2 H_2$, as regularly as the boiling point does.

The evident connection between all these acids is very interesting, as it accounts for their frequent occurrence in nature, more or less mixed together. Thus, in butter, which contains much oleic acid, we find four of these acids in small quantity, and it is remarkable that these four are not successive, but alternate in the series, the number of eq. of carbon and hydrogen being in them divisible by 4. They are, butyric acid, C_4 ; caproic acid, C_6 ; caprylic acid, C_8 ; and capric acid, C_{10} . Redtenbacher observes, that the baryta salts of these four acids all form prisms, and that they are less soluble as the acid rises in the series; while the baryta salts of the intermediate acids, whose eqs. of carbon are divisible by 2, all crystallize in scales, and also diminish in solubility in ascending the scale. These curious facts furnish almost the only means of separating these acids from each other.

When oleic and elaidic acids are heated with potash there are produced acetic acid and a new fatty acid, $C_{12} H_{20} O_2$, $H O$. The difference between the formula of this acid and that of oleic acid is equal to 3 eq. acetic acid, which accounts for its production. Again, elaidic acid, $C_{12} H_{18} O_2$, plus 7 eq. oxygen, yields 2 eq. of the new acid, and 2 eq. acetic acid. This acid only differs from palmitic (ethalic) acid by 1 eq. hydrogen.

ACIDS OF CASTOR OIL.

Castor oil is a very peculiar oil. When saponified, it yields two fat acids, one crystallizable, margaritic acid; the other liquid, ricinic acid. The latter is little known. The former is said to be $C_{25} H_{51} O_2$. Castor oil is a mixture of the compounds of glycerine with these two acids. It is soluble, when pure, in its own bulk of alcohol. Nitrous acid converts it into a solid crystallizable fat, palmine, analogous to elaidine, but differing from it.

When castor oil is acted on by nitric acid, it yields a new volatile oily acid, of an agreeable aromatic odor, which is called cœnanthylic acid, as its formula is that of cœnanthic acid, plus 1 eq. oxygen; $C_{14} H_{15} O_3$, $H O$. It forms an ether of a very agreeable aromatic smell. In the residue is found suberic acid.

Palmine, the fat formed by the action of nitrous acid on castor oil, is a white crystalline fat, which, when saponified, yields glycerine and a fatty acid, palmic acid, not yet fully investigated, but said by Playfair to belong to the series of margaryle, that is, to differ from margaric acid only in oxygen. A current of sulphurous acid passed through castor oil is said to produce palmine, or at all events a fat which yields palmic acid. This, if true, is a very singular fact, since nitrous acid, an oxidizing agent, and sulphurous acid, a deoxidizing one, would thus produce the same result.

NATURAL FATS AND FIXED OILS.

These are all compounds of glycerine with fatty acids. When heated with alcalies they yield soaps; with oxide of lead, plasters; while in both cases glycerine is set free. The most common of all these compounds are stearine, margarine, and oleine, of which always two, and often all three, are present, stearine predominating in the hard, margarine in the soft, and oleine in the liquid fats. It is only the compounds of glycerine with volatile acids, such as butyric acid, that have a strong smell.

There are two kinds of fat oils: the fat oils proper, and the drying oils. The latter contain much oleine, the oleic acid of which is different from the usual oleic acid, and they absorb oxygen from the air, drying into a kind of varnish. When oils become rancid, they are partly decomposed; and, generally, some of the acid, as well as of the glycerine, is set free, while oxygen is absorbed. Pure stearine, margarine, and oleine do not become rancid, and that change depends on a process of decay or slow oxidation going on in the impurities of the oil, and from them passing to the oil itself.

ACTION OF HEAT ON OILS AND FATS. ACROLEINE.

When oils are distilled they produce a variety of compounds, such as margaric acid, sebacic acid, margarone, carbohydrogens, &c. &c., and one most remarkable compound, acroleine, derived from glycerine.

Acroleine, $C_3H_4O_2$, is best obtained by distilling glycerine with phosphoric acid. The whole operation must be carried on in vessels full of carbonic acid gas, as the acroleine is very rapidly oxidized by the air. Its vapor attacks the eyes and nose in a most painful, indeed intolerable, degree. It may be considered as the hydrated oxide of a radical C_3H_3 , (acryle, analogous to acetylene) $C_3H_3, O + H_2O$, analogous to aldehyde. It rapidly absorbs oxygen and forms acrylic acid, $C_3H_3O_3, H_2O$, analogous to acetic acid. In certain circumstances, the solution of acroleine exposed to the air deposits a white solid, $C_{10}H_7O_4$.

The presence of acroleine among the products of the distillation of an oil or fat is a convincing proof of the presence of glycerine in that oil. It is worthy of remark that glycerine, $C_3H_7O_3$, is hydrated oxide of acryle, plus 3 eq. water, so that oils and fats may be called compounds of acroleine as well as of glycerine. It is even conceivable that acroleine may be C_3H_3O , which we have seen to be a probable form of glycerine in some fats; or that the glycerine in these fats may be acroleine, as above given, $C_3H_4O_2$, and that when this glycerine is separated by an alkali, it takes up 3 eq. of water.

Castor oil, so peculiar in other respects, exhibits a peculiar decomposition by heat. It yields acroleine, and a volatile oil, composed

of two oils insoluble in alkalies ; besides some saponifiable acids. When about one-fifth has been distilled, the residue suddenly consolidates into a spongy, yellow, elastic mass, insoluble in all menstrua except caustic alkalies, with which it forms peculiar soaps. These, when decomposed by an acid, yield a tough viscid substance having the characters of an acid. The product of the distillation again distilled with water, yields several oily compounds, one of which is crystalline, and not yet fully studied. The less volatile residue being again distilled yields a peculiar crystalline fatty acid, and another oily acid. Neither of these has been properly investigated.

When oils or fats are decomposed at a red-heat, they yield much combustible gas (oil gas), formed of olefiant gas and marsh gas, and several liquid carbohydrogens : in particular, benzole, $C_{12}H_6$, Faraday's quadricarburetted hydrogen, C_4H_4 , or C_6H_6 , and another isomeric compound, which is only liquid at very low temperatures.

ACTION OF SULPHURIC ACID ON FAT OILS.

Sulphuric acid, if added in small quantity to oils, combines with their glycerine ; but if used in excess gives rise to a number of new products. In the first instance there are formed, when a mixture of oleine and margarine is acted on, two new acids, sulpholeic acid and sulphomargaric acid. These acids have not been isolated, but when their solution in water is heated, the sulphuric acid separates, and the oleic and margaric acids are transformed into four new acids, metamargaric and hydromargaric acids, and metoleic and hydroleic acids. The two former are solid, crystallizable, and partly volatile. A compound of the two exists, which acts like a single acid, and has been called hydromargaric acid ; it is also a fusible solid. The two latter are oily, and all five appear to be bibasic. Their composition cannot be considered as ascertained, but the three first are nearly allied to margaric acid.

It would lead to confusion here to mention the different formulæ proposed by Frémy, Berzelius, and Liebig, for these acids, more especially when it is considered that we have no sufficient evidence of the perfect freedom from foreign admixture of the acids analyzed, and that the recent observations of Miller show an amount of variation in the melting points which leads to the suspicion of impurity. The subject is interesting, but difficult, and requires a very minute investigation.

Metoleic and hydroleic acids, when distilled, yield water, carbonic acid, and two carbohydrogens, oleéne and elaéne, both of which contain carbon and hydrogen in an equal number of equivalents ; oleéne is supposed to be $C_{10}H_{10}$, and elaéne, $C_{18}H_{18}$; but this is not established.

ACTION OF NITROUS ACID ON FAT OILS.

Nitrous acid, or solution of nitrate of mercury, as already mentioned, causes fat oils to become solid, converting oleine into elaidine. This curious change takes place in olive oil, almond oil, rape-seed oil, hazel-nut oil, castor oil and others: but the drying oils, such as oils of linseed, hemp-seed, walnut, poppy-seed, &c., are not at all affected by nitrous acid. In all the oils which are changed into elaidine, except in castor oil, the product is the same. It is the formation of this solid fat which causes the mercurial ointments, made with nitrate, to become hard when kept. The elaidine, when purified by pressure and crystallization in alcohol and ether, yields neither margaric nor oleic acid when saponified, but only elaidic acid, isomeric with oleic acid. There is probably a secondary reaction, for a red coloring matter is also formed, which has not been investigated.

Castor oil, as has been already mentioned, yields, with nitrous acid, a new fat palmine, which contains a new acid, palmic acid. These resemble elaidine and elaidic acid, but are quite distinct.

ACTION OF BASES ON FAT OILS. SOAPS AND PLASTERS.

When fat oils are boiled with solution of caustic alkalies, they are gradually dissolved in the water, if there be not too great an excess of alkali present, forming ropy or gelatinous solutions, which gelatinize on cooling. These are solutions of soaps, that is, potash and soda salts of the fatty acids, along with the glycerine set free. In order to have the soaps in a solid form, the solutions are boiled down, and when the alkali reaches a certain concentration, the soap becomes insoluble, and rises to the surface in a soft, half-melted state. This is drawn off into moulds, and the mass formed on cooling, is soap. Another method of causing the soap to separate from the water in which it is dissolved, consists in adding sea-salt, which at once coagulates the soap, converting it into a soap of soda, if it is a soap of potash. Of course, the glycerine, in both cases, is carried off in the mother liquid. Such is the theory of soap-making, which is very simple, depending on the affinity between the alkalies and the fat acids; on the solubility in water of the alkaline stearates, margarates, oleates, palmitates, &c.; and, finally, on the power of a certain amount of free alkali or sea-salt, to coagulate the soap, and render it insoluble in the liquid in which it swims, and which in fact runs off its surface as water does off the surface of fat, while yet the soap retains perfectly its solubility in pure water.

The soaps of lime, baryta, &c., are insoluble in water, and have no detergent power: hence the waste occasioned by using hard, that is, calcareous, water for washing. All the salts of lime in such water must first be entirely precipitated in the form of curdy flocculi, before any soap can be dissolved so as to act as a detergent.

The soaps of potash are soft, compared with those of soda, which are called hard soaps. White soap is stearate, with some oleate of soda. Naples soap is oleate and margarate of potash. Common soft soap is chiefly oleate of potash, but as it is made from whale oil or seal oil, it contains also phocenate of potash, which gives it a disagreeable smell.

Castile soap is oleate and margarate of soda, colored by metallic oxides, chiefly oxides of iron, in such a way as to give the desired mottled appearance. Much and excellent soap is now made of palm oil, and is, therefore, palmitate of soda.

Soaps are soluble in alcohol, forming tincture of soap, which is an admirable liniment for bruises, and is much used along with laudanum, as tincture of soap and opium; also with camphorated spirit, forming opodeldoc.

Plasters are soaps of certain metallic oxides, chiefly oxide of lead, which are insoluble in water, but fusible, and possess useful properties. Litharge plaster is made by boiling finely 5 parts of powdered oxide of lead with 9 parts of olive oil and some water, till the combination is complete. It is plastic at ordinary temperatures, and melts when heated. When solution of acetate of lead, is added to solution of soap, plaster, that is, olente and margarate of lead, is precipitated. When prepared in this way, it becomes hard. White lead plaster, made with carbonate of lead, is very plastic and fusible, and is much used. Iron plaster and mercurial plaster are of small importance.

The chief liquid fat oils and drying oils of the vegetable kingdom have already been mentioned. In the animal kingdom, there are fish oils, characterized by containing phocanine; also cod liver oil, &c. &c.

The solid oils or fats of the vegetable kingdom are, butter of cacao (*theobroma cacao*); of nutmeg (*myristica moschata*); of coconut (*cocos nucifera*); of laurel (*laurus nobilis*); palm oil (*avoiira olais*; *elais guianensis*); galam butter (*bassia butyracea*); and some others. Those of the animal kingdom are tallow, or suet, butter, hog's lard, human fat, &c.

Spermaceti is a peculiar fat found in the head of *physeter macrocephalus*. When purified from a small quantity of a liquid oil, it constitutes cetine, which is a compound of ethal, (hydrated oxide of cetylc,) with cetylic acid, or at least yields those compounds when boiled with potash. Cetine crystallizes beautifully when melted or when dissolved in hot alcohol. Cetine, when acted on by nitric acid, yields first, pimelic acid, $C_7H_6O_4$; which is then oxidized into adipic acid, $C_{14}H_{12}O_{10}$. Thus, $2(C_7H_6O_4) + O_4 = C_{14}H_{12}O_{10}$. The adipic acid is finally converted into succinic acid; thus, $2(C_{14}H_{12}O_{10}) + O_{11} = 7(C_4H_2O_4) + 3HO$.

Cholesterine is a fat found in bile, and also, in small proportion, in the blood, and in much larger quantity as an ingredient of

cerebral matter. It forms the chief ingredient of biliary calculi. It dissolves in hot alcohol, crystallizes on cooling, in silvery scales, but cannot be saponified by boiling with potash. Its formula is either $C_{26}H_{42}O$, or $C_{26}H_{42}O$. When acted on by nitric acid, it yields a new acid, cholesteric acid, which contains nitrogen, probably as nitrous acid.

Ambreine, a fat analogous to cholesterine, is found in ambergris. It yields, with nitric acid, ambreic acid. Castorine is a similar fat found in castoreum.

Wax is another peculiar fatty body, the origin of which is derived from flowers, whence it is collected by the bee. It melts at about 150° . It is a mixture of two fats, cerine and myricine, the former soluble, the latter insoluble, in hot alcohol. Cerine is partly saponified by boiling with potash, yielding apparently margaric and oleic acids (?) along with a neutral fat, ceraine having the same composition as myricine. There are several kinds of vegetable wax, but they are all much more easily saponified than bees-wax. When bees-wax is distilled, it yields neither acroleine nor sebacic acid, and would therefore appear to contain neither oleic acid nor glycerine. When heated with nitric acid, wax is almost entirely converted into succinic acid.

Japan, or tree-wax, is a true fat, composed of palmitic acid and glycerine without oleine. When acted on by nitric acid it yields first pimelic and adipic acids, and then succinic acid, as in the case of spermaceti.

Cerosine is the name given to a waxy substance occasionally found on the surface of the sugar-cane. It is not saponifiable, and appears to contain $C_{26}H_{42}O_2$.

Athamantine, from the root of *athamanta oreoselinum*, is a crystalline fat-like body, containing valerianic acid, united to a body, oreoselone, which supplies the place of glycerine in the neutral athamantine. Oreoselone is $C_{14}H_{22}O_2$, that is, isomeric with dry benzoic acid. Athamantine is $C_{24}H_{38}O_7 = C_{14}H_{22}O_2$ (1 eq. oreoselone) + $C_{10}H_{16}O_4$ (1 eq. valerianic acid). Athamantine combines with hydrochloric acid, and the compound, when boiled with water, deposits crystals, which are oreoselone plus water = $C_{14}H_{22}O_4$, and isomeric with crystallized benzoic acid.

Having now briefly described the best known organic acids, it is necessary to mention a number of acids, found in the analyses of different vegetables, but not yet sufficiently studied to decide whether they exist independently, or may not rather be, in many cases, identical with some of the acids above described. Such are chelidonic acid, lately shown by Lerch to be analogous to meconic acid, and to have the formula $C_{14}H_{18}O_{12} = C_{14}H_{18}O_{10} \cdot 3H_2O$, cainic, crameria, caffeic, boletic, fungic, tanacetia, lactucic, atropic, cocognidic, solanic, conic, aceric, moroxylic, kinovic, and menispermic acids, besides others.

VOLATILE OR ESSENTIAL OILS.

These oils are so called because they are obtained by distillation of vegetables, generally along with water, and because, having in most cases the concentrated odor of the plant, they are usually called essences. Most of them exist ready-formed in the plant, which owes its smell to them: but some, as oil of bitter almonds and oil of spiræa, are formed by a kind of fermentation, excited in the case of the former, as already stated, by the contact of amygdaline, emulsine and water.

Many plants, when cut, yield balsams, which are mixtures of essential oils and resins. In many essential oils a crystalline matter is deposited, called a camphor or stearoptene. They are all soluble in alcohol. Many absorb oxygen from the air and become acid, as oil of cinnamon. They are violently acted on by nitric acid and iodine, chlorine, bromine, &c.

They may be divided into three kinds: 1st, those containing only carbon and hydrogen, as oil of turpentine; 2d, those containing also oxygen, as oil of cloves; 3d, those containing sulphur, as oil of garlic.

1. NON-OXYGENATED ESSENTIAL OILS.

Almost every one of these (which constitute a very numerous class of oils) as yet accurately analyzed, has been found to contain carbon and hydrogen in the proportion $C_{10}H_8$, or what is the same thing, C_5H_4 , or $C_{20}H_{16}$. The following are the most important.

Oil of turpentine, $C_{10}H_8$, or $C_{20}H_{16}$, is obtained by distilling, with water, turpentine, the juice extending from many species of *pinus*. Rosin, resin, or colophonium, remains in the retort. The oil has a peculiar smell, and burns with a smoky flame. Its Sp. G. is 0.86. It boils at 312° . Strong nitric acid sets fire to it, and it is also decomposed with flame by chlorine. It dissolves sulphur, phosphorus, and fat oils. When exposed to hydrochloric acid gas, it combines with it, forming a white crystalline solid like camphor, and a liquid compound. The solid is $C_{10}H_7Cl = C_{20}H_{15}, HCl$. When heated with lime, it yields a pure oil, dadyle, $C_{20}H_{16}$. The liquid hydrochlorate, heated with lime, yields another pure oil, pencyle, rather more volatile than dadyle, but having the same composition. Oil of turpentine would seem to be composed of pencyle and dadyle, both $C_{10}H_8$; the former giving a liquid, the latter a solid compound, with hydrochloric acid.

Nitric acid, by long boiling, converts oil of turpentine into an acid, turpentic acid, $C_{14}H_9O_7, HO?$

Oil of turpentine is used in medicine, internally, as a vermifuge, especially in cases of the larger worms, such as *tenia*; externally, as a stimulant and counter-irritant. In the arts it is used for resins in making varnishes.

Oil of juniper has the same composition as oil of turpentine, but possesses its own peculiar odor, which it communicates to alcohol in gin. This oil is diuretic.

Oil of savine has the same composition. It is also diuretic. Oil of elemi has the same composition, and a pleasant odor. Oil of storax, or styrole, appears to have the composition of $C_2 H$, or some multiple of it. Nitric acid acts on it, producing hydrocyanic acid, benzoic acid, and a fragrant crystalline body, nitrostyrole. Styrole itself is a very remarkable substance, differing as it does from all the other non-oxygenated oils. Dr. Blyth has been for some time engaged in its investigation, and has obtained very interesting results, not yet ready for publication.

Oil of lemons has the probable composition, $C_8 H_4$. Like oil of turpentine it is composed of two isomeric oils, citrene and citrylene, which combine with hydrochloric acid, forming a liquid and a solid compound, decomposed by heating with lime. The solid camphor seems to be, $C_{10} H_8 Cl = C_{10} H_8, H Cl$. The oils of cedro, cedrat, oranges, and limes, are all essentially identical with oil of lemons. Oil of neroli, or of orange-flower, is quite distinct, having the odor of the flower, while the others have that of the rind of the fruit. Its composition is not accurately known.

Oil of copaiva is another isomeric form of oil of turpentine, which it very much resembles, forming a camphor with hydrochloric acid. It is diuretic, and much used in affections of the bladder and urethra. Oils of pepper and of cubebs are still of the same composition in 100 parts, although the latter is supposed to be $C_{15} H_{13}$.

2. OXYGENATED ESSENTIAL OILS.

The principal oils of this class have been already considered, their radicals being known. These are oil of bitter almonds, or hyduret of benzoyle; oil of spirœa, or hyduret of salicyle; oil of cinnamon, or hyduret of cinnamyle; oil of cloves (eugenic acid); oil of cumine, or hyduret of cumyle; oil of aniseed, the solid part of which is $C_{10} H_{12} O_2$, and with nitric acid yields anisic acid, and other compounds already described at p. 448; oil of valerian, chiefly valerianic acid, &c. The essence of valerian, according to Gerhardt, generally contains several compounds, especially if old. When fresh, it contains no valerianic acid, but an oil, valerole, which is crystallizable, and soon passes into valerianic acid in the air. This oil is $C_{12} H_{10} O_2$, and is isomeric with metacetone, also with Kane's oxide of mesityle, and with oxide of allyle (see oil of garlic, p. 470). Besides valerole, the essence contains a carbohydrogen, borneène, $C_{10} H_8$, identical with the oil obtained from Borneo camphor; and finally, a camphor, which is identical with Borneo camphor.

Oil of cinnamon, according to Mulder, is, when quite fresh, $C_{11} H_{11} O_2$. It rapidly attracts oxygen, and $3 (C_{11} H_{11} O_2) + O_2 =$

1 eq. cinnamic acid, 1 eq. resin alpha, $C_{15}H_8O$, 1 eq. resin beta, $C_{20}H_{16}O_4$, and 6 eq. water H_2O . With hydrochloric acid it yields two different resins, $C_{20}H_{16}O$, and $C_{14}H_7O$, besides other products. With oil of vitriol it yields two more resins, $C_{20}H_{16}O_2$, and $C_{20}H_{16}O$, which together are equal to 3 eq. of the oil minus 3 eq. water. With nitric acid the fresh oil forms a crystalline compound, $C_{15}H_8NO_7 = C_{15}H_8O_3 + NO_3 + H_2O$. With water this body yields hyduret of cinnamyle, $C_{15}H_8O_2$. If dissolved in sulphuric acid and mixed with water it gives cinnamic acid, $C_{15}H_7O_3$. Along with the crystals, nitric acid yields a red oil, which, with water, gives another oil, $C_{15}H_7O_2$.

Oil of anise, $C_{20}H_{18}O_2$, yields with bromine a compound in fine crystals, $C_{20}\left\{\begin{matrix} H_2 \\ Cl_2 \end{matrix}\right. O_2$. When acted on by strong acids, or by the chlorides of tin or antimony, oil of anise is converted into an isomeric body, anisone, analogous to benzoine.

Of the remaining oils of this class may be mentioned the oils of dill, of fennel, of parsley, of carraway, of coriander, of pimperl, of peppermint ($C_{10}H_{10}O$, or $C_{10}H_{10}O_2$; this oil yields several new compounds with chlorine), of marjoram, of lavender, rosemary, basil, thyme, rue ($C_{20}H_{18}O_3$), cascarilla, chamomile, wormwood, tea, cardamom, nutmeg, cajeput, rhodium, rose (otto or attar of roses), bergamot, saffron, sassafras, and sweet-bay ($C_{20}H_{18}O$). Of these, little certain is known, and almost all require a careful study.

The oil of sassafras, $C_{10}H_8O_2$, when cooled, deposits very large and beautiful crystals, measuring $1\frac{1}{4}$ inches on the side. With bromine, the solid essence yields crystals, composed of $C_{10}HBr_4O_2$.

The oil or essence of *semen contra* is said to be $C_{15}H_{15}O_2$. That of *artemisia dracunculus*, or essence of estragon, yields, when treated with sulphuric acid, anisoine, identical with that of oil of anise, and in fact contains the same oxygenated oil (stearoptene of anise), along with a different carbohydrogen. Laurent has obtained from essence of estragon a series of new compounds. He represents the essence by $C_{20}H_{20}O_2$; but Gerhardt has shown that it is identical with oil of anise, and that draconic acid and dracole are the same as anisic acid and anisole. The acid is $C_{14}H_7O_3$, H_2O .

The concrete essence of the tonka bean is called coumarine. It is very fragrant, and its formula is $C_{15}H_8O_4$. Potash changes it first into cumaric acid, $C_{15}H_7O_3$, H_2O , and afterward into salicylic acid; and hot nitric acid converts it into nitropicric acid. Cold nitric acid produces a white volatile crystalline solid, $C_{15}\left\{\begin{matrix} H_2 \\ NO_2 \end{matrix}\right. O_4$. Coumarine also combines with chloride of antimony, forming yellow crystals.

3. SULPHURETTED ESSENTIAL OILS.

This class of oils is distinguished by a pungent peculiar smell, and acrid burning taste, as in oil of mustard, or an intense alliaceous odor, as in oil of garlic or of onions. The more important of them have been lately investigated, and have yielded very striking results.

Essence of mustard is prepared from mustard-seed in the same way as oil of bitter almonds from that seed. The seed is macerated with water and afterward distilled, when it yields an oil of a most remarkable nature, containing not only sulphur, but also nitrogen. The pure oil is colorless, of Sp. G. 1.010, and boils at 298° or 300° . Its formula is $C_8 H_5 N S_2$, so that it contains no oxygen. With ammonia it forms a crystalline compound, which is, in fact, an organic base or alkali, thiosinamine = $C_8 H_5 N_2 S_2$. This is a bitter compound, which forms, like nearly all organic bases, crystalline compounds with chloride of platinum and chloride of mercury.

Thiosinamine, acted on by dry oxide of lead or of mercury, loses all its sulphur, forming a new base, sinamine = $C_8 H_5 N_2$, = $C_8 H_5 N_2 S_2 - 2 HS$. It is, therefore, thiosinamine, minus 2 eq. sulphuretted hydrogen, which have acted on the oxide of lead, forming water and sulphide of lead. Sinamine forms definite compounds with chlorides of mercury and platinum. It is a powerful base, and very bitter to the taste.

When oil of mustard is acted on by moist hydrated oxide of lead, it loses both sulphur and carbon, in the proportion CS_2 , forming sulphide of lead and carbonate of lead, along with a new base, sinapoline, which dissolves in hot water, in alcohol, and in ether. Its formula is $C_{14} H_{12} N_2 O_2$; and it is formed from 2 eq. oil of mustard, with 6 eq. oxide of lead and 2 eq. water, as follows: $2 (C_8 H_5 N S_2) + 6 Pb O + 2 H O = C_{14} H_{12} N_2 O_2 + 4 Pb S + 2 (Pb O, C O_2)$.

When oil of mustard is acted on by an alcoholic solution of potash, there is separated neutral carbonate of potash; and the addition of water causes the separation of an oily liquid, which is in its relations analogous to oil of mustard. It appears to be $C_{18} H_{15} N_3 S_4 O_4$. By the action of baryta upon it, sulphide of barium is formed, and a basic compound not farther examined. The liquid from which this oil has separated contains the potassium salt of a very remarkable acid, which forms with a salt of lead the compound $C_8 N H_5 S_4$, Pb, = $C_8 H_5 N S_2, HS + Pb S$. These compounds are produced as follows: 6 eq. oil of mustard, 10 of water, and 2 eq. of potash, $6 (C_8 H_5 N S_2) + 10 H O + 2 K O$, yield 1 eq. of the new oil, $C_{18} H_{15} N_3 S_4 O_4$, 1 eq. ammonia $N H_3$, 4 eq. carbonic acid, $C_4 O_2$, and 2 of the new salt of potassium, $2 (C_8 H_5 N S_4, K)$. It is probable, however, that the first change is more simple, and that 3 eq. oil of mustard, 5 of

water, and 1 of potash, yield 1 eq. of an oil, $C_{14}H_{14}N_2S_2O_2$, 2 eq. carbonic acid, C_2O_4 , and 1 of the potassium salt $C_8H_8NS_4$, K. Two eq. of the oil $C_{14}H_{14}N_2S_2O_2$, lose 1 eq. ammonia, and give rise to the oil $C_{12}H_{12}N_2S_4O_4$.

These very interesting facts, important in a high degree from their bearing on the theory of organic bases, are taken from a paper by Dr. Will, lately published, to which I refer the reader. Dr. Will points out some curious relations. Thus sinapoline, $C_{14}H_{14}N_2O_2$, may be derived from 2 eq. of oil of mustard and 6 eq. water, which yield 1 eq. sinapoline, 2 eq. carbonic acid, and 4 eq. sulphuretted hydrogen. If we now suppose 2 of the 4 eq. of HS to combine with 1 eq. sinapoline, they will produce the oil, $C_{14}H_{14}N_2O_2S_2$, which is supposed to be first formed and afterward to lose ammonia: while, if the 2 other eq. of HS combine with 1 eq. of unchanged oil of mustard they will form the acid of the new potassium salt: $C_8H_8NS_2 + 2HS = C_8H_7NS_4$.

Again, synapoline may be viewed as hyduret of benzoyle, plus 2 eq. ammonia, $C_{14}H_8O_2$, $2NH_3$; and the hypothetical oil is then $C_{14}H_8O_2$, $N_2H_8S_2$, or hyduret of benzoyle, plus 2 eq. sulphide of ammonium.

The separation of the elements of bisulphide of carbon from oil of mustard, and the simultaneous formation of a series of basic compounds, would indicate that oil of mustard might be a compound of sulphocyanogen; since sulphocyanide of ammonium, when heated, gives off bisulphide of carbon, and gives rise to a series of basic compounds, melamine, ammeline, &c. Now it is very remarkable that oil of mustard admits of being considered as $C_8H_8 + C_2NS_2$, that is, the sulphocyanide of a new radical allyle, C_8H_8 ; of which, as we shall presently see, oil of garlic is the sulphide. Finally, oil of mustard may be a compound of hydrocyanic acid with the hydrosulphide of sulphide of acryle: $C_8H_8S, HS + C_2NH$. Its very pungent smell and powerful action on the eyes certainly rank it beside acroleine, C_3H_2O , HO. The researches of Wertheim have lately demonstrated the truth of the supposition above mentioned, and the oil of mustard, or sulphocyanide of allyle, has been formed artificially from the oil of garlic, the sulphide of allyle, and *vice versa*.

Oil of mustard contains an indifferent nitrogenized body, myrosine, which, analogous to emulsine, yields the essential oil, after maceration of the seed with water, and fermentation. The fermentation of myrosine is prevented in the same way as that of emulsine, namely, by coagulation. The seeds also contain a crystalline body, sinapisine, resembling a fat. The substance, which, along with myrosine, yields the oil, appears to be myronic acid, or rather myronate of potash, a body not yet fully studied. The seeds of *sinapis alba* contain the myrosine, as sweet almonds contain emulsine; but, being destitute of myronic acid or myronate

of potash, as sweet almonds are of amygdaline, they yield none of the oil.

It has very recently been shown by Hubatka and Wertheim, that the essential oils of *cochlearia armoracia*, (horse-radish), *cochlearia officinalis*, and *alliaria officinalis*, consist almost entirely of oil of mustard, although the latter oil has also a very strong smell of oil of garlic, an oil which has not been discovered in it.

The essential oil of garlic, from the bulbs of *allium sativum*, is a peculiar sulphurized compound. Wertheim has lately studied it, and shown that it is the sulphide of a new radical, allyle = $C_3H_5 = All$, and its formula is $C_3H_5, S = All S$. The crude oil contains a little of a higher sulphide, possibly $All S_2$, and also some of the oxide of allyle, $C_3H_5O = All O$, which is an oily liquid of an offensive smell. The radical allyle appears to enter into numerous combinations, and, among others, Wertheim analyzes the following: the sulphide or pure oil of garlic, $All S$; the compounds of that sulphide with the sulphides of platinum, palladium, and silver, $5 All S + 6 Pt S_2$; $2 All S + 3 Pt S_2$; $2 All S + 3 Pd S$; and $x All S + Ag S$? double compounds with the sulphides and chlorides of mercury and platinum; $3 (All S + Pt S_2) + (All Cl + Pt Cl_2)$; and $(All S + 2 Hg S) + (All Cl + 2 Hg Cl)$; and lastly nitrate of the oxides of silver and allyle, $(All O + Ag O) + NO_5$. Our space does not permit us to do more than point out the existence of these curious compounds.

The essential oil of assafoetida appears to consist of at least two oils, one of which, if not both, contains sulphur. It has a very offensive odor. It does not combine with ammonia like the oil of mustard. Dr. Douglas MacLagan finds, as might be expected from the odor, that one of the oils it contains is sulphide of allyle.

The essential oils of hops, of water pepper, and of *arum maculatum*, are believed to contain sulphur.

CONCRETE VOLATILE PRINCIPLES, ALLIED TO THE ESSENTIAL OILS.

There are several substances which may be classed under this head; such as hellenine, from *inula helenium*, which is a volatile crystalline solid, $C_{15}H_{10}O_2$. With nitric acid it yields nitrohellenine, $C_{15} \begin{Bmatrix} H_9 \\ N O_4 O_2 \end{Bmatrix}$. When distilled with anhydrous phosphoric acid, hellenine loses 2 eq. water, yielding hellenène, a carbohydrogen, $C_{15}H_8$. With chlorine, it yields the compound, $C_{15} \begin{Bmatrix} H_9 \\ Cl O_2 \end{Bmatrix} + HCl$.

Asarone, from *asarum europæum*, is a volatile solid, having a remarkable tendency to crystallize in beautifully defined forms, and also to pass into the amorphous condition, from which it may be again brought into the crystalline state. Schmidt has very recently

studied its crystallization under the microscope, and has obtained results which are most interesting in reference to the formation of crystals in general. I must refer to his elaborate paper in the "Annalen der Chemie und Pharmacie," for February, 1845. Its composition is, $C_{20}H_{13}O_5$.

Anemonine, from various species of *anemone*, is a volatile, crystallizable solid, the formula of which is $C_5H_2O_2$. It forms with oxide of lead a compound, $3(C_5H_2O_2) + PbO$. With bases it yields anemonic acid, the composition of which is unknown.

Cantharidine, the active principle of Spanish flies, is a volatile acrid solid, the composition of which is $C_{10}H_8O_4$.

The following plants, *epidendron vanilla*, *quassia amara*, *tangkonia madagascariensis*, *primula auricula*, and *primula veris*, contain concrete volatile essences not yet analyzed.

CAOUTCHOUC, OR GUM ELASTIC.

Caoutchouc is a substance *sui generis*, which in composition approaches more nearly to the essential oils than to any other class of compounds. It is the coagulated or inspissated juice of many tropical trees, the chief of which is *siphonia elastica* (*iatropha elastica*, *hevea guianensis*). The juice, as it flows from the tree, is made to dry on moulds of clay, which are afterward broken out, leaving a bottle of caoutchouc. It is generally blackened by smoke, but when pure it is white and transparent. It is highly elastic, and the freshly cut surfaces adhere strongly if pressed together. It is insoluble in water, alcohol, and acids; but it dissolves in ether, naptha, coal-tar naptha, bisulphide of carbon, and essential oils. Its solutions in ether and coal-tar naptha, when dried up, leave the caoutchouc in an elastic state. On this principle water-proof cloth is made. Caoutchouc is much used in chemical operations to form flexible connecting tubes.

When exposed to heat, caoutchouc first melts, and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbohydrogens. Some of these oils boil at 90° , others at 680° , and at intermediate points. I found that one highly rectified oil, which boiled at 96° , and had the composition of olefiant gas, when acted on by sulphuric acid, yielded an oil which boiled at 428° , and had the same composition. But most of these oils have the composition of oil of turpentine, $C_{10}H_8$ or $C_{10}H_{10}$. One of these, called caoutchine, gives with chlorine an oil, $C_{10}H_8 + Cl$.

RESINS.

Resins are generally found along with essential oils, and many of these oils, by the action of the air, are converted into resins. In this change, the essential oils lose a part of their hydrogen, which is converted into water, and take up some oxygen besides.

In fact, the resins, as a class, are acid bodies. They are insoluble in water, but become soft in boiling water. They dissolve in alcohol, and often crystallize from that solvent.

The acid resins combine with bases; their salts with the alcalies are called resinous soaps. The resins are not volatile, although very inflammable. They are purified from essential oils by distilling off the latter along with water; but, as thus obtained, they are generally mixtures of several resins.

Turpentine and colophony, or common resin. Turpentine is the semifluid juice which exudes from many species of *pinus*. When distilled with water, it yields oil of turpentine, $C_{10}H_{16}$ or $C_{10}H_{14}$, while colophony or resin remains behind, which is $C_{10}H_7O$, or $C_{10}H_{12}O_4$, or, more accurately, $C_{10}H_{10}O_4$. Here the oil, $C_{10}H_{16}$, has lost 2 eq. hydrogen, replaced by 2 eq. oxygen, $C_{10}H_{10}O_2$, and this compound, like aldehyde, has taken up 2 eq. of oxygen to form the acid resin, $C_{10}H_{10}O_4$.

Colophony contains two different resins: resin alpha, or pinic acid, and resin beta, or sylvic acid. The latter is said to be $C_{10}H_{14}O_2$, the former, isomeric with it, $C_{10}H_{10}O_4$; and their properties are very similar, being those of colophony, which is formed of them. The sylvic acid is crystallizable.

When distilled with lime, colophony yields two oily liquids, resineone, $C_{12}H_{18}O$, and resinone, $C_{10}H_{16}O$.

The resin of copaiva is $C_{10}H_{10}O_4$, according to Rose; but there is some reason to believe that it is isomeric with the preceding. A variety of it has occurred, containing $C_{10}H_{14}O_2$, and when combined with oxide of lead, $C_{10}H_{12}O_4$. This resin crystallizes.

The resin of elemi contains two resins, one crystallizable. Both are said to be $C_{10}H_{16}O_2$. Anime also contains two resins. Euphorbium yields a resin having the same composition as elemi. Benzoin contains, besides benzoic acid and a volatile oil, three resins, alpha, $C_{10}H_{14}O_4$; beta, $C_{10}H_{12}O_2$; and gamma, $C_{10}H_{10}O_2$. The resin alpha contains the sum of the other two, and by long boiling with carbonate of soda, which dissolves the resin gamma alone, is resolved into them.

Balsam of tolu contains, besides essential oil, benzoic and cinnamic acids, and a carbohydrogen, $C_{11}H_{12}$, a resin, $C_{11}H_{10}O_2$. It contains the elements of benzoic ether, plus 1 eq. oxygen. When the balsam is distilled, *per se*, it actually yields benzoic ether, along with a new carbohydrogen, called benzoène, or toluole, $C_{11}H_8$. This last compound yields with sulphuric acid a new acid, $C_{11}H_7S_2O_5 + 3H_2O$; and, with nitric acid, two new nitrogenized compounds, $C_{11} \begin{cases} H_7 \\ NO_4 \end{cases}$, called protonitrobenzoène, or nitrotoluide, analogous to nitrobenzide, and another, binitrobenzoène, $C_{11}H_5 + 2NO_2$. The former is isomeric with salicylamide, and with anthranilic acid, and, like the latter body, when heated with lime,

yields aniline. When acted on by hydrosulphide of ammonia, it yields another artificial base, toluidine. With chlorine, benzoëne also yields several new products.

Styracine, the resin of styrax, is $C_{24}H_{11}O_2$. When acted on by nitric acid, it yields the products of decomposition of cinnamic acid.

When fluid storax is distilled with water, it yields a remarkable oil, styrole, $C_{10}H_8$, which is also formed by the action of heat on cinnamic acid, and is probably derived from cinnamic acid present in the storax.

Styrole, when heated to 400° in a closed tube, changes into a solid glassy mass of the same composition in 100 parts, but the formula of which is $C_{14}H_7$. It is called metastyrole. By a stronger heat, it is volatilized and reconverted into the oil. Styrole is analogous to benzole and toluole, and like them, forms compounds, when acted on by nitric acid, in which H is replaced by N O. — (*Hoffmann and Blyth*).

The resin of guaiacum is remarkable for its tendency to become blue by the contact of many different substances. It contains two resins, but their composition is not ascertained. Lac contains four resins, besides coloring matter. Dammara, mastic, dragon's-blood, and sandarach, are resins much used in making varnishes.

Jalap contains two resins; one, a soft resin soluble in ether, $C_{12}H_{18}O_{11}$; and an acid resin insoluble in ether, which, from striking a fine red color with sulphuric acid, is called rhodeoretine, $C_{12}H_{18}O_{10}$. When combined with bases, it takes up 1 eq. water, forming hydrorhodeoretine, very similar to rhodeoretine, but soluble in water, $C_{12}H_{20}O_{11}$. When rhodeoretine is acted on by hydrochloric acid, it is resolved into grape sugar, $C_{12}H_{12}O_{12}$, and an oily liquid rhodeoretinole, $C_{30}H_{42}O_8$. This reaction places rhodeoretine near to salicine and phloridzine. On the other hand, if we compare 7 eq. of starch, $7(C_{12}H_{10}O_{10}) = C_{84}H_{70}O_{70}$ with 2 eq. rhodeoretine, $2(C_{12}H_{18}O_{10}) = C_{24}H_{70}O_{40}$, we can see how this resin may be formed from starch, &c., by deoxidation. Rhubarb contains 3 resins, aporetine, phæoretine, and erythreoretine. The two first are both $C_{16}H_8O_7$; the third is $C_{16}H_8O_7$. They are accompanied by an intensely yellow crystallizable acid, chrysophanic acid, $C_{10}H_8O_3$, or $C_{20}H_{16}O_{12}$. This latter substance is also found in lichens, such as *parmelia parietina*, *squamaria elegans*, &c. Copal, which of all the resins is the most insoluble, is said to contain five. Copal varnish is made by adding hot oil of turpentine to copal fused at a gentle heat.

Turf or peat contains several resinous bodies, examined by Mulder. In the turf of Friesland he found four resins: alpha, $C_{80}H_{100}O_8$; beta, $C_{77}H_{87}O_8$; gamma, $C_{104}H_{104}O_8$; and delta, $C_{131}H_{131}O_8$. A lighter kind of turf from another locality yielded two resins; alpha, $C_{85}H_{105}O_8$; and gamma, $C_{80}H_{104}O_8$.

Resinous varnishes are made by dissolving resins in oil of turpentine and other essential oils, or in drying oils. Spirit varnishes are made by dissolving resins in very strong alcohol.*

ACTION OF HEAT ON RESINS.

When resins are distilled in close vessels, they yield a great deal of gas of a high illuminating power, and many volatile liquid compounds of carbon and hydrogen.

Pinic acid yields, when heated, colophonic acid. Colophony yields resineine, an oil, $C_{20}H_{15}O$; also retinaphtha, $C_{14}H_8$, which with chlorine forms a compound $C_{14}H_8Cl_2$; retinylène, $C_{10}H_{12}$, which with sulphuric acid yields an acid, isomeric with sulphocumenic acid, $C_{10}H_{11}S_2O_5, H_2O$; retinole, $C_{28}H_{18}$; and finally a solid product, retisterène, fusible at 152° , having the same composition as naphthaline, $C_{10}H_8$.

COLORING MATTERS CONTAINING NO NITROGEN.

1. YELLOW COLORING MATTERS.

The following are the most important of the yellow vegetable coloring matters, many of which are used in dyeing.

Curcumine, from the root of *curcuma longa*, is resinous, and is dissolved by alkalies, which change it to brown. Hence it is used as a test for alkalies, under the name of turmeric. Gamboge yellow is extracted from gamboge, the dried juice of *garcinia gambogia*. It is resinous and powerfully purgative. Annatto or anatto is obtained from the seeds of *bixa orellana* and *metella tinctoria*. Carotene is the coloring matter of the carrot, *daucus carota*. Rhabarberine is a name formerly given to the yellow acid of rhubarb, now called chrysophanic acid, which is found also in lichens as above stated. It has great coloring power, and yields a fine violet with alkalies. It is fusible and volatile: formula, $C_{10}H_8O_5$. From occurring in *parmelia parietina*, it has also been called parietine and parietinic acid. Luteoline, the coloring principle of *reseda luteola* or woad, is volatile and crystallizable. Quercitrine, from the bark of *quercus tinctoria*, is crystalline, and its composition is $C_{16}H_{12}O_7, H_2O$. Other yellow coloring matters are, morine, from *morus tinctoria*; safflower yellow, from *carthamus tinctorius*; polychroite from saffron, and others of less interest.

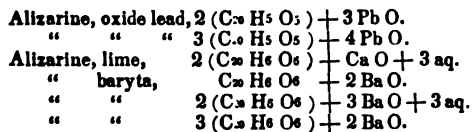
* Resins and Resinoids were formerly supposed to contain the active medicinal agents of all plants, but recent investigations have proven that the medicinal activity of plants resides in a number of principles, among which *resins*, *neutral principles*, and *alkaloids* are prominent. The firm of B. KERR & Co., New York, are the most successful investigators in this branch of medical chemistry, and therefore manufacture reliable preparations from the organic kingdom. The firm of MERRILL & Co., of Cincinnati, and several other firms, are now making reliable preparations, which are coming into extensive use, not only in the Eclectic but the Allopathic ranks.—S.

2. RED COLORING MATTERS.

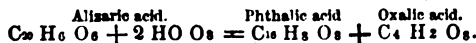
Draconine, or dragon's blood, is a red gum resin, from *dracæna draco*. It is much used to color varnishes. Santaline, the coloring matter of *pterocarpus santalinus*, is also resinous, and has an intense red color. Anchusine, from *anchusa tinctoria*, is the source of the color of alkanet; it is resinous, and yields violet vapors when heated. Carthamine is the red coloring matter of safflower, *carthamus tinctorius*. It is a very fine and intense red, much used for dyeing rose color, for pink saucers and for rouge, at least the *rouge végétale*.

Madder, the root of *rubia tinctorium*, contains three different red coloring matters, madder purple, red, and orange. All three are volatile, and the sublimed crystals of madder red, which are of a fine orange-red color, are called alizarine. This is the substance which yields the Turkey red dye. With alkalies it yields purple or violet color, with acids yellow. When dissolved in hot water or alcohol, alizarine yields rose-colored solutions. The composition of pure madder red is unknown.*

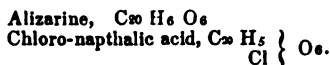
* Wolf and Stricker have obtained from madder pure *purpurine* and *alizarine*. The hydrated alizarine, on being heated, fuses and sublimes into orange-colored needles, insoluble in cold water, but dissolves in boiling water, imparting to it a deep yellow color. The smallest trace of alkali colors this solution red, (a test for alkali ?) They are soluble in alcohol and ether. The alcoholic solution is reddened by alkali, but not the ethereal solution. Alkalies dissolve alizarine, the solution being red by transmitted light, and blue by reflected light. The composition of alizarine is $C_{15}H_8O_4$. The compounds of alizarine are :



The conversion of *alizaric* into *phthalic* and *oxalic acids* by equation .



The above furthermore demonstrate, that Laurent's chloro-naphthalic acid is identical with chlorinated alizarine :



Purpurine crystallizes from its strong alcoholic solution in red needles, but the crystals from weak alcohol are fine soft orange-colored needles drying to a felted mass. These latter crystals lose water at 100°. Purpurine is more soluble in water than alizarine, and imparts to the fluid a deeper red color. It fuses with heat, and finally sublimes, with a carbonaceous residue. In caustic potassa it is cherry-red without the blue reflection of alizarine. Its formula is anhydrous $C_{12}H_6O_6$; and the hydrous $C_{12}H_6O_6 + HO$. As purpurine contains two equivalents less of carbon than alizarine, it is probable

Hæmatoxyline is the red of logwood, *hæmatoxylum campechianum*. It is soluble in water and alcohol, and yields orange crystals, which give to water a red color, brightened by acids, and turned to a violet or blue by alcalies. With alum, logwood yields various shades of violet; with an iron mordant, gray and black. Black cloth and hats are dyed with it, which is the reason they are reddened by acids. According to Erdmann, pure hæmatoxyline is pale yellow, and is colored red by the atmosphere. Its formula he found to be $C_{40}H_{17}O_{15}$. When acted on by ammonia it yields hæmateine, which is dark red, and forms with excess of ammonia a splendid purple matter. Hæmateine is $C_{40}H_{15}O_{16}$; and the purple compound with ammonia is $C_{40}H_{15}O_{16} + 2NH_3 + aq$. Brazilwood and Camwood yield coloring matters very similar to hæmatoxyline, if not identical with it.

Many flowers contain a red coloring matter, which is turned green by alcalies, and is very fugitive. It is soluble in water and alcohol.

3. BLUE COLORING MATTERS.

These are chiefly found in flowers and fruits. They are very closely allied to the red of flowers and fruits, which are no doubt often derived from them by the action of acids. They are all turned green by alcalies, and red by acids. Such blue coloring matters as are more permanent contain nitrogen, and will be considered hereafter.

4. GREEN COLORING MATTER.

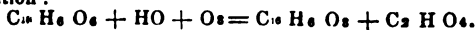
Chlorophyll. — This is the green of leaves. It is of a nature allied to that of wax, soluble in ether and alcohol, insoluble in water. It is very neutral or indifferent in its relations to other substances.

Polychrome is the name given to a peculiar crystalline principle found in some vegetables, such as quassia. It gives to water the quality of exhibiting a curious play of colors, among which blue predominates, like that of the opal, when the solution is viewed by reflected light; 1 part will give this property to 1,500,000 of water. Its formula is said to be $C_{46}H_8O_9$, H_2O , which is the same as that of quercitrine, and contains 2 eq. of oxygen more than the aporetine of rhubarb.

NON-AZOTIZED VEGETABLE COMPOUNDS, THE NATURE OF WHICH IS NOT YET ASCERTAINED.

In this subdivision may be included a number of compounds, most of which crystallize and have a bitter taste, but are neutral, and cannot yet be referred to any particular series of compounds.

that, by oxidation, the latter may be converted into the former, as shown by the equation :



With nitric acid, purpurine yields phthalic and oxalic acids, as is shown by the above equation, where, by the absorption of eight equivalents of oxygen, the alizaric acid is converted into anhydrous, phthalic and oxalic acids.—S.

Salicine, phloridzine, and rhodeoretine, which would formerly have been here described, are now treated of along with substances allied to them. The substances now to be briefly mentioned have usually been termed the bitter and extractive principles of plants.

Gentianine, from *gentiana lutea*, forms yellow needles, very bitter. Menyanthine, from *menyanthes trifoliata*, is bitter, but does not crystallize. Absinthine, from *artemisia absinthium*, or wormwood, is a semi-crystalline mass, very bitter, soluble in alcohol. Tanacetine, from *tanacetum vulgare*, is very similar to it. Santonine is a beautifully crystallizable compound, obtained from *artemisia contra*. It is soluble in alcohol, bitter to the taste, volatile, and colored yellow by the action of light. Populine, from the bark and leaves of *populus tremula*, forms white crystals, of a sweetish and acrid taste, colored red by sulphuric acid. It may possibly be connected with salicine. Liriodendrine is a crystalline bitter substance, from the bark of *liriodendron tulipifera*. Picrolichenine is an intensely bitter crystalline compound, found in the lichen *variolaria amara*. It is principally febrifuge. In contact with ammonia and without the access of air, it is changed into a reddish-yellow matter, which finally deposits yellow crystals, not bitter. With access of air, it yields with ammonia a deep red very soluble matter. Cetrarine is another bitter principle, from the lichen *cetraria islandica*, or Iceland moss. It is colored deep blue by hydrochloric acid. It is said also to be febrifuge. Ilicine, from *ilex aquifolium*, forms brownish yellow crystals, very bitter and febrifuge. Syringine is the bitter principle of the lilac, *syringa vulgaris*. It is crystalline and soluble in alcohol. Daphnine is a bitter crystalline substance, obtained from *daphne mezereum*. Hesperidine is a crystalline body, found in the spongy envelop of oranges and lemons. Elaterine is the active principle of *momordica elaterium*, is crystalline, bitter, and very purgative. Its formula is $C_{20}H_{14}O_5$. Colocynthine, the active principle of colocynth, is amorphous, intensely bitter and purgative. Bryonine, from *bryonia alba* and *dioica*, is similar in its properties. Mudarine is the emetic principle of *calotropis mudarii*. It is a brown amorphous matter, the solution of which in water gelatinizes at 95° , and becomes again liquid on cooling. Scillitine is the bitter of *scilla maritima*. It is amorphous, bitter, purgative and emetic. Cathartine is the bitter purgative principle of senna. Antiarine, $C_{14}H_{14}O_5$, is the active principle of the poison called *upas antiar*. It is, when introduced into a wound, especially along with soluble matters, such as sugar, a most powerful poison, and hitherto no means are known by which its fatal action can be arrested.

Zanthopierine is a bitter crystalline substance from the bark of *zanthoxylum clava herculis*. It has been little studied. Picrotoxine, the bitter principle of *menispermum cocculus* (*cocculus indicus*), forms white prisms. The composition of these is not certain, and recent researches seem to show that picrotoxine is a vegetable base,

and contains nitrogen, like all that class of compounds. Columbine is a crystalline bitter substance, obtained from columba, the root of *menispermum palmatum*, and somewhat analogous to picrotoxine. Quassine is a yellow, crystalline, and very bitter substance from the wood of *quassia amara*. Its formula is said to be $C_{22}H_{12}O_6$. Lupuline, the bitter principle of hops, is not crystallizable. Lactucine is a crystalline resinoid bitter substance, from the juice of *lactuca virosa* (*lactucarium*). It has anodyne properties. Ergotine is an uncrystallized brown powder, extracted from ergot of rye by hot alcohol, after the fatty matters have been removed by ether. It appears to be poisonous, and is probably the active matter of the ergot. Porphyroxine is a crystallizable substance found in Bengal opium. Its solution in diluted acids becomes red when boiled. It requires further investigation. Saponine is a peculiar principle, found in the root of *saponaria officinalis*. It is white, amorphous, and has a taste first sweet, then styptic, and finally acrid. It is a powerful sternutatory. It is soluble in water, and its solution, even when much diluted, froths when agitated, like a solution of soap. The root is used as a detergent. When acted on by alkalies, it is converted into an acid, saponic acid, $C_{22}H_{22}O_{13}$. Asparagine, $C_4H_7N_2O_5 \cdot 2H_2O$, is a crystallizable substance found in asparagus, in *althæa officinalis*, and in other plants, especially those grown in the dark. When boiled with alkalies it loses ammonia, NH_3 , and forms aspartic acid, $C_4H_7NO_5 \cdot 2H_2O$, which is a bibasic acid. The crystals of asparagine are very large, colorless, and transparent, also hard and brittle. Not only alkalies, but acids and ferments transform it into aspartic acid and ammonia. Smilacine is a crystalline substance, found in *smilax sarsaparilla*. Its composition is $C_{15}H_{13}O_5$. In *China nova* there is found a substance very analogous to smilacine, the composition of which is $C_{15}H_{12}O_4$; that is, smilacine, minus 1 eq. water. Senegguine is an acrid and astringent substance, found in *polygala senega*. It excites sneezing powerfully: formula, $C_{22}H_{18}O_{11}$. Guaiacine appears to be the active principle of guaiacum. It is acrid and bitter. Plumbagine, extracted from the root of *plumbago europæa*, forms yellow prisms, the taste of which is first sweet and styptic, then acrid and hot. The yellow color of its aqueous solution is turned cherry-red by alkalies. Cyclamine is a crystalline matter from the root of *cyclamen europæum*. It is very acrid, purgative, and emetic. Peucedanine is a very acrid crystalline principle derived from the root of *peucedanum officinale*: formula, C_4H_2O . Imperatorine, $C_{21}H_{12}O_5$, is a crystallizable compound, obtained from the root of *imperatoria ostruthium*. It is very acrid and styptic. Phillyrine, from the bark of various species of *phillyrea*, crystallizes in silvery scales, which are bitter. Fraxinine, from the bark of *fraxinus excelsior*, is a crystallizable bitter principle. Tanghine is a similar substance from *tanghinia madagascariensis*. It is poisonous.

Melampyrine is a tasteless, neutral, crystalline substance, from *melampyrum nemorosum*. Meconine is a neutral, crystalline compound contained in opium. It is soluble in water, alcohol, and ether. It is acrid to the taste, fusible and volatile: formula, $C_{10}H_8O_4$. With nitric acid it yields nitromeconine or nitromeconic acid, $C_{20}H_8NO_{12}$. As meconine may be $C_{20}H_{10}O_2$, nitromeconine is $C_{20} \begin{cases} H_9 \\ NO_4 \end{cases} O_2$; in which 1 eq. hydrogen is replaced by 1 eq. nitrous acid. Chlorine transforms meconine into crystals containing chlorine, which, however, by the action of alcalies, yield an acid free from chlorine, mechloic acid, $C_{14}H_7O_{10}$?

Cubebene, $C_{24}H_{17}O_{10}$, is a crystalline compound contained in cubebs. Olivile, $C_{18}H_9H_4$, is a crystallizable acrid substance, found in the gum of the olive-tree. Olivine is another crystalline matter found on the leaves of the same plant. It is bitter. Onicine is a crystalline matter, found in *centaurea benedicta*, and in the numerous family of the *cynarocephaleæ*. It is neutral and bitter, and very similar to columbine. Its formula is $C_{28}H_{18}O_{10}$, or $C_{28}H_{17}O_{15}$? and in some respects it approaches to salicine and phloridzine; but it requires further investigation. Limonine, or limone, a bitter crystalline matter found in the seeds of oranges, lemons, &c., is $C_{28}H_{23}O_{13}$, when reduced to 42 eq. carbon. This would be enicine, minus 2 eq. water. Angelicine is a crystallized compound found in angelica root.

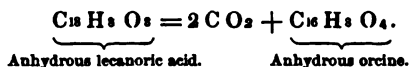
Besides the above, which have merely been briefly catalogued for want of space, at least an equal number of substances, chiefly crystallizable, and either bitter, acrid, or in a few cases tasteless, have been extracted by various chemists from many different genera and species of plants, but have been so little examined hitherto that we cannot safely describe them as distinct and peculiar.

NITROGENIZED COLORING MATTERS, AND ALLIED SUBSTANCES.

There are several fine and valuable colors, which contain nitrogen as an essential element, and probably in the form of ammonia or amide. Such colors are archil, litmus, and cudbear, derived from certain species of lichens; and indigo, derived from the juice of various plants, especially different species of *indigofera*. All these colors are derived from colorless compounds, frequently of an acid nature, by the combined action of air and ammonia. Of these colorless substances, the most important are, lecanoric acid, erythric acid, and orceine.

1. *Lecanoric Acid*, or lecanorine, occurs in *lecanora tartarea*, *variolaria lactea*, and other lichens. It is extracted by ether, along with another acid, parellic acid, and a fatty matter colored green by chlorophyll. It forms minute white crystals, insoluble in water, soluble in alcohol and ether. Its formula is $C_{15}H_8O_3$, $HO = C_{15}H_8O_2$. When heated to 212° it becomes anhydrous,

$C_{18}H_8O_8$. When heated with alcalies, such as baryta, a carbonate is deposited, and a sweet substance remains dissolved, which crystallizes on evaporation. This is orcine, which is formed along with carbonic acid, according to the following equation:



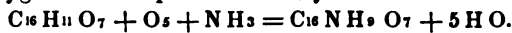
The same change takes place when lecanoric acid is boiled with water, and for this reason orcine alone is obtained when the lichens are extracted by that solvent.

By the combined action of air and ammonia, lecanoric acid is gradually changed into a deep rich blue or purple mass. Here orcine is first produced, and by the action of ammonia on that compound, orceine, the blue compound, is formed. When heated, lecanoric acid yields a sublimate of anhydrous orcine. When boiled with alcohol, it is gradually converted into the following compound.

2. *Lecanorate of Oxide of Ethyle. SYN. Pseudoerythrine of Heeren; Erythrine of Kane.*—This compound is formed when lecanoric acid and the lichens containing it are boiled with alcohol. It is soluble in hot water, from which it crystallizes on cooling, and the solution, after long boiling, contains orcine. It may be sublimed unchanged, and when boiled with alcalies it yields alcohol, carbonic acid, and orcine. Its true nature was discovered by Schunck, who also first detected lecanoric acid. Its formula is $C_{18}H_{12}O_8 = C_4H_8O + C_{14}H_4O_8$.

Lecanorate of oxide of methyle is analogous to the preceding compound.

3. Orcine forms large transparent crystals, is very soluble in water, and has a sweet taste. When anhydrous, it may be distilled unchanged. When mixed with ammonia, and exposed to the air, it gradually acquires a deep blood-red color, forming a nitrogenized coloring matter, orceine, soluble in ammonia with a deep red, in fixed alcalies with a rich violet color, the formula of which is $C_{16}NH_8O_7$. The production of anhydrous orcine from lecanoric acid, by boiling with baryta, or even by boiling with water, has been described above. But the crystals of orcine, as deposited from its aqueous solution, are a hydrate, $C_{16}H_{11}O_7 = C_{16}H_8O_4 + 3H_2O$. It is this hydrate which, with the addition of 5 eq. of oxygen, and 1 eq. of ammonia, yields orceine and water.



Orcine forms with oxide of lead a compound, the formula of which is $C_{16}H_8O_4 + 3PbO$.

4. *Parellic Acid.*—This acid accompanies lecanoric acid. It forms either minute crystals, the formula of which is $C_{18}H_8O_8$,

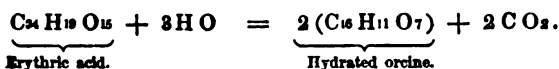
or large hydrated crystals, which are transparent and of great density. The formula of the latter is $C_{21}H_2O_{11} = C_8H_2O_5, H_2O$. When heated to 212° , both kinds lose water, and become $C_8H_7O_5$, which is probably the formula of the anhydrous acid.

With ammonia, parrellic acid becomes brown, and when heated with fixed alkalies, it yields carbonic acid, and other products, not investigated.

5. *Erythric Acid*. *SYN.* *Erythrine of Heeren; Erythriline of Kane; Orcino-lecanoric Acid*.—This acid is found in *parmelia roccella*, and *roccella tinctoria*, the latter being the lichen which yields the best archil. It may be extracted by hot water and purified by alcohol. It crystallizes from alcohol in stellated groups. Its solutions are decomposed by boiling, yielding a bitter compound, picroerythrine. When heated it yields a sublimate of orcine, and when boiled with alkalies it is resolved into carbonic acid and orcine. When boiled with alcohol, it yields lecanorate of oxide of ethyle. All these facts indicate a close relation to lecanoric acid, and Schunck, who discovered the erythric acid, has pointed out that its formula, $C_{34}H_{19}O_{15}$, represents a compound of 1 eq. lecanoric acid and 1 eq. orcine. It is probably, therefore, a coupled acid, orcino-lecanoric acid.



It combines with 4 eq. of oxide of lead, three of which probably unite with the orcine, and the fourth with the lecanoric acid. When boiled with alcohol, it is resolved into lecanoric acid, which unites with oxide of ethyle, and orcine, which is found in solution. It must also yield orcine in large quantity when boiled with baryta, in which case it loses 2 eq. of carbonic acid, and takes up 3 eq. of water.



In other words, the orcine, ready formed, is separated, and the lecanoric acid undergoes the change formerly described.

Erythric, or orcino-lecanoric acid, is the most important of all the principles found in lichens; but from the facility with which it is altered by boiling with water or alcohol, but little of it can be extracted unchanged. When acted on by ammonia, so as to yield the blue matter of orchil, the lichens containing this acid obviously yield a large proportion of the compound of orceine with ammonia, on which the color depends. Hence their superior quality.

Variolarine is the name given to a substance obtained by Robiquet, from *variolaria dealbata*. It has been little studied, and is probably identical with some of the compounds above described.

6. *Picroerythrine*. *Syn. Erythrin-bitter of Heeren; Amarythrine of Kane*. — This compound is formed when erythric acid, or the lichens containing it, are boiled with water, and is the cause of the bitter taste of the decoction. When boiled with baryta, it yields orcine and carbonate of baryta, and when heated, it yields a sublimate of orcine. This is easily explained by its formula, which is $C_{24}H_{24}O_{20}$, that is, erythric acid, plus 5 eq. of water. For the exact knowledge of all the preceding substances we are indebted to the recent researches of Schunck.

7. *Usnic Acid*. — This acid is found in many lichens, such as *lichen rangiferminus*, and in many species of *usnea*, *ramalina*, *parmelia*, *biatora*, *leccidea*, *alectora*, *evernia*, and *cladonia*. It is extracted by ether, and forms sulphur yellow crystals, insoluble in water and alcohol. Like the other acids of the lichens, it yields colored compounds under the influence of air and ammonia or fixed alkalies; but these appear to contain no nitrogen, and are not blue or purple, but red. It cannot be made to yield orcine, so far as is yet known. Its formula is $C_{28}H_{17}O_{14}$, which corresponds to 2 eq. of lecanoric acid, plus C_2H_2 , and minus O_2 .

9. *Chrysophanic Acid*. — This is another crystallizable acid found in *parmelia parietina*. It forms golden-yellow crystals, and with alcoholic solutions of potash and ammonia, yields a splendid red color. Its formula is $C_{10}H_2O_2$, that is $\frac{1}{2}$ of $(C_{20}H_{10})$ naphthaline, plus 3 eq. of oxygen. Its salts are blue or violet when dry, red in solution. This acid has also been found in rhubarb by Schlossberger and Doepping. This and the preceding acid were discovered in the lichens by Rochleder and Heldt.

9. Archil contains, according to Kane, two blue compounds, which he calls alpha-orcine and beta-orcine, $C_{28}H_{10}N O_2$, and $C_{18}H_{10}N O_2$; besides a third, of an acid nature, *erythroleic acid*, $C_{28}H_{22}O_4$.

10. Litmus contains, according to Kane, a red fluid, erythroleine, $C_{28}H_{22}O_4$; and three solids, of a purple color, erythrolitmine, $C_{28}H_{22}O_{18}$; azolitmine, which contains nitrogen, and is the principal constituent of litmus; and spaniolitmine, $C_{18}H_7O_{11}$. According to Gélis, litmus contains three coloring matters, one soluble in ether, which is orange-red; one soluble in alcohol, blood-red, and one soluble in water. The second is the chief ingredient of the dye. All give blue compounds with alkalies.

11. *Phloridzine* is the deep blue compound formed from phloridzine by the action of air and ammonia. Its formula is $C_{28}H_{22}N_2O_{28}$.

12. INDIGO.

This valuable dye has been long known; but it is only since 1827 that its chemical relations have been accurately studied. No substance in the whole range of chemistry has yielded a greater

variety of most interesting products; and the study of the metamorphoses of indigo has already thrown much light on the laws of the decomposition of organic substances. For what is known on this subject, we are indebted, first, in point of time, to Chevreuil, Runge, Walter Crum, Liebig, Berzelius and Dumas; more lately, and in an especial manner, to the comprehensive researches of Erdmann, Fritzsche, and Laurent; the last of whom has made known several interesting series of new compounds derived from indigo, and has both confirmed and extended, as well as corrected, in some cases, the previous results obtained by Erdmann; still more recently, Hoffmann and Muspratt have greatly extended our knowledge of the derivatives of indigo.

Indigo is obtained from various plants, chiefly of the genus *indigofera*, as *I. tinctoria*, *anil*, *argentea*, &c, but also of other genera, as *nerium*, *isatis*, *pergularia*, *gymnema*, *polygonum*, *tephrosia*, *amorphia*, and others. In the juice of these plants, it exists in the form of a colorless soluble compound, probably a compound of white indigo with an alkali. When exposed to the air, it is converted into the blue compound, and becomes at the same time insoluble, just as in an artificial solution of white or reduced indigo in an alkali. The manufacture of indigo is not thoroughly understood, but it would appear that ammonia, as well as air, contributes to the formation of the color, probably by converting into white indigo some compound present in the fresh juice, the nature of which, however, is still uncertain. In the Antilles, in the East Indies, the leaves are made to ferment in water, during which much ammonia is formed, and the indigo is found in the soluble state, ready to become blue and insoluble by absorbing oxygen. But in North America, the dried leaves are infused in warm water, or boiled with water till the liquid becomes green, when, on exposure to the air, it deposits blue insoluble indigo. Here the same change must, in great part at least, have taken place during the drying, as during the fermentation of the other process.

The indigo of commerce is a deep blue powder, often cohering in cakes, and exhibiting, when polished by rubbing with the nail or any hard substance, a coppery color and lustre. It is tasteless and inodorous, insoluble in water, and nearly so in alcohol and ether. It may be purified by treating it successively with boiling diluted sulphuric acid and with water, which remove a glutinous matter; with aqua potassa, at a gentle heat, which dissolves a brown coloring matter; and with boiling alcohol, which takes up a red coloring matter. When fresh alcohol becomes no longer red, but blue, the indigo is as pure as it can be made by such means.

To purify it still farther, it is digested with water, lime, and grape or starch sugar, which deoxides or reduces the indigo, while the lime combines with the reduced indigo, forming a soluble compound, of a wine-yellow tint. This being filtered into dilute hydrochloric

acid, which removes the lime, deposits pure indigo as a blue powder. Cloth steeped in the above solution of indigo, and exposed to the air, is quickly dyed blue, as the indigo, at the moment of being rendered insoluble, combines with the fibre of the cloth, to which it adheres very firmly, so that it cannot be washed away. If indigo, grape sugar, soda and alcohol be digested together in proper proportions, a yellow solution is obtained, which when exposed to air, deposits pure indigo in crystals. — (*Fritzsche*).

Pure indigo, when rapidly heated on a slip of platinum, volatilizes, yielding purple vapors, which condense in purple crystals on a cold surface. These crystals are called indigotine; but they are nothing else than sublimed indigo, and have all the chemical characters of pure indigo. When distilled, indigo yields, among other products common to all nitrogenized organic matters, a very curious oily liquid, of powerfully basic properties, and forming salts with acids which crystallize with singular facility. This base is aniline, (benzidam, crystalline, kyanol,) and is found in the oil of coal-tar, as well as in the products of distillation of many nitrogenized bodies.

Oil of vitriol dissolves indigo with a deep blue color, forming two blue acids. This solution is much used in dyeing. Nitric acid, chloric acid, chromic acid, chlorine and bromine, all dissolve indigo, giving rise to oxygenized and chlorinized or brominized products, all of which are yellow and orange-colored. When boiled with strong aqua potassa, indigo is also oxidized and dissolved in the form of new acids.

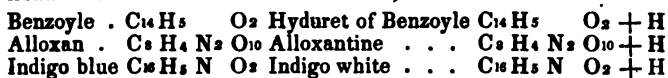
When placed in contact with deoxidizing or reducing agents, such as protosalts of iron, tin, and manganese, or honey and grape sugar, along with an alkali, such as soda or lime, indigo is decolorized and dissolved in combination with alkali. The addition of diluted hydrochloric acid, air being carefully excluded, precipitates reduced or white indigo.

White or reduced indigo, $C_{16}H_5NO_2$, obtained as above described, is a crystalline powder of a dirty white, which, if washed with water previously boiled to expel air, and cooled in closed vessels, and dried in vacuo, is bluish externally, but gray within. The blue parts being removed, the remainder is reduced indigo. When moist, it very rapidly passes into blue indigo, oxygen being absorbed: when dry, the change is more slowly effected. It is insoluble in water and acids, very soluble in alkaline solutions; its solutions, if exposed to the air, deposit pure indigo blue, as a powder.

The first accurate analysis of indigo blue was made by Walter Crum; and his results have been confirmed by all succeeding experimenters. The formula now adopted for indigo, as agreeing best with its numerous metamorphoses, is one first proposed by Dumas; namely, $C_{16}H_5NO_2$. This formula is the same with

that of cyanide of benzoyle, or of benzile, $C_{14}H_5O_2 + C_2N = C_{16}H_5NO_2$.

The relation of white indigo to blue indigo is, according to one view, the same as that of hyduret of benzoyle to benzoyle, or of alloxantine to alloxan. Thus we have,



According to another hypothesis, white indigo is the hydrate of an inferior degree of oxidation of the same radical of which blue indigo is the higher oxide. Blue indigo, on this view, is $C_{16}H_5N + O_2$, and white indigo is a hydrate, $C_{16}H_5N + O + H O$. This latter view is the more probable, not only in regard to indigo, but also in regard to alloxan, for, assuming uryle to be $C_8N_2O_4 = Ul$, alloxan will be $Ul + O_2 + 4 H O$, and alloxantine will be $Ul + O + 5 H O$.

The action of grape sugar, in reducing indigo, tells in favor of the latter hypothesis. For if white indigo is blue indigo plus hydrogen, this hydrogen, is derived from water, the oxygen of which must have combined with the hydrogen of the sugar (to convert the sugar into formic acid, which is produced in this operation). Here, then, we should have oxygen leaving hydrogen to combine with hydrogen, or, in other words, water produced and decomposed at the same time, which is in the highest degree improbable. To demonstrate this, let the radical of indigo be assumed to be anyle = $C_{16}H_5N = An$: let blue indigo be $An O_2$ and white indigo $An O_2, H$, or $An O, H O$. Then 12 eq. of blue indigo, 12 of water, and 1 of grape sugar, act on each other, and, according to the view which makes white indigo the hyduret of blue indigo, the reaction is as follows: $12 An O_2 + 12 H O + C_{12}H_{12}O_{12} = 12 (An O_2, H) + 6 (C_2 H O_2) + 6 H O$. In this explanation it is evident that 6 eq. of oxygen have quitted hydrogen to combine with hydrogen. On the other view, the reaction is as follows, free from any such absurdity: $12 An O_2 + 12 H O + C_{12}H_{12}O_{12} = 12 An O, H O + 6 (C_2 H O_2) + 6 H O$. Here the 12 eq. of deutoxide of anyle (blue indigo) lose 12 eq. oxygen, which are replaced by 12 eq. water; and the 12 eq. oxygen acting on the sugar, 6 eq. take 6 eq. hydrogen, forming water, and 6 eq. convert the residue into formic acid. The student will bear in mind that $C_2 H O_2$ is the formula of formic acid, and $C_{12}H_{12}O_{12}$ that of dry grape sugar.

We shall therefore consider white indigo as the hydrated protoxide of anyle ($C_{16}H_5N, O + H O$.) and blue indigo as the anhydrous deutoxide ($C_{16}H_5N, O_2$). White indigo forms compounds with bases, in which, no doubt, its hydratic water is replaced by an equivalent of metallic oxide, as in the general formula, $C_{16}H_5N, O + M O$.

ACTION OF SULPHURIC ACID ON INDIGO.

When powdered pure indigo is added to 15 parts of oil of vitriol, and gently warmed, a deep blue solution is formed, which mixes perfectly with water. But if only 8 or 10 parts of acid are used, the addition of water causes the deposition of a purple powder, while a blue solution is obtained. The purple powder, which, although insoluble in dilute acid, is soluble in pure water, is sulphopurpuric acid; the blue solution contains two acids, sulphoindigotic and hyposulphoindigotic acids. When neutralized with potash, these acids form salts, which separate from the liquid when it is saturated with any alkaline salt, such as acetate or carbonate of potash. The two blue salts may be separated from each other by alcohol, but the composition of the hyposulphoindigotate of potash is not known. The sulphoindigotate appears to be strictly a hyposulphoindigotate, and its formula is in all probability $C_{16}H_4NO_2, S_2O_3 + KO$. Here the indigo has lost 1 eq. of hydrogen, and the 2 eq. sulphuric acid 1 eq. oxygen. Dumas' view, according to which the salt is a double sulphate, analogous to sulphovinate of potash, $C_{16}H_4NO, SO_3 + KO, SO_3$, is not supported by the chemical relations of these substances. Dumas conjectured that indigo blue was analogous to alcohol, and that its formula was $C_{16}H_4N, O + HO$, the body $C_{16}H_4N, O$, being analogous to oxide of ethyle. But, as already stated, this view is far-fetched, and does not agree with the chemical relations of indigo. It would make, for example, white indigo $C_{16}H_4N, O + H + HO$, or $C_{16}NH_4 + 2HO$, both must improbable formulæ.

The blue solution of indigo in oil of vitriol, if diluted and digested with flannel or woollen cloth, is entirely deprived of blue color, while the cloth is so effectually dyed that the color cannot be washed out. It can, however, be dissolved from the cloth by carbonate of ammonia, and by this means the sulphoindigotates of ammonia, and from these the other salts of the blue acids, are prepared.

The sulphopurpuric acid, according to Dumas, contains the elements of 2 eq. sulphuric acid and 2 eq. indigo, and neutralizes only 1 eq. of base. But the indigo in it has probably lost hydrogen, (while the acid has lost oxygen), or hydrogen and oxygen.

PRODUCTS OF THE OXIDATION OF INDIGO.

Isatine, $C_{16}H_5NO_4$. — This interesting compound, which is blue indigo plus 2 eq. oxygen, is formed by digesting indigo along with water, sulphuric acid, and bichromate of potash, or by heating indigo with weak nitric acid. It dissolves, and the solution on evaporation deposits aurora-red crystals of isatine, sparingly soluble in cold water, more soluble in hot water and in alcohol. By the action of chlorine, it yields two compounds in which hydrogen

is partially replaced by chlorine. It may be volatilized if heated on a plate of metal. When acted on by a strong solution of potash, isatine is dissolved with an intense violet color, which on addition of water and evaporation changes to yellow, and the liquid deposits pale yellow crystals, which contain potash, united to a new acid, isatinic acid, formed from isatine by the addition of 1 eq. water. When separated from its salts by stronger acids, isatinic acid is at once resolved into isatine and water; but if isatinate of lead be decomposed by sulphuretted hydrogen, and the filtered solution evaporated spontaneously in vacuo, the acid is obtained as a white flocculent powder, which, when dissolved in boiling water, instantly becomes red, and the solution on cooling deposits crystals of isatine. Isatinic acid is $C_{16}H_5NO_5HO$. Its salts have the formula $C_{16}H_5NO_5, MO$. The violet-colored compound first formed when isatine acts on potash, is a compound of isatine and potash, which, when heated with water, soon passes into isatinate of potash. With sulphurous acid, or rather sulphites, isatine forms salts of the formula $C_{16}H_5NO_4, 2SO_2 + MO$; which may be formed also by the action of sulphurous acid on isatinates.

By the action of chlorine, isatine is converted into two compounds, chlorisatine and bichlorisatine. When chlorine is passed through isatine or indigo suspended in water, both these compounds are formed, and they are separated by crystallization, chlorisatine being the least soluble of the two.

Chlorisatine, $C_{16}\left\{\begin{smallmatrix} H^4 \\ Cl \end{smallmatrix}\right. NO_4$, forms transparent orange-yellow four-sided prisms, isomorphous with isatine, and very analogous to it in all respects. When acted on by potash, there is first formed a deep red solution, which when heated soon becomes yellow, and on cooling deposits brilliant pale yellow crystals of chlorisatinate of potash, $C_{16}\left\{\begin{smallmatrix} H^5 \\ Cl \end{smallmatrix}\right. NO_5, KO$, a salt perfectly analogous to isatinate of potash, and containing an acid, chlorisatinic acid, which is chlorisatine plus 1 eq. water, $C_{16}H_5ClNO_5$. Like isatinic acid, when separated from its salts it is speedily resolved into chlorisatine and water. Chlorisatinate of silver, $C_{16}\left\{\begin{smallmatrix} H^5 \\ Cl \end{smallmatrix}\right. NO_5, AgO$, forms yellow crystals, soluble in hot water. Chlorisatinate of baryta, $C_{16}\left\{\begin{smallmatrix} H^5 \\ Cl \end{smallmatrix}\right. NO_5, BaO, + 3aq.$, forms golden yellow tables. Chlorisatinate of lead, $C_{16}\left\{\begin{smallmatrix} H^5 \\ Cl \end{smallmatrix}\right. NO_5, PbO$, when first precipitated from the salt of potash by nitrate of lead, forms a gelatinous yellow precipitate, which soon becomes flocculent, acquiring a splendid scarlet color. The red salt is crystalline, the yellow amorphous. Chlorisatinate of copper forms at first a brownish yellow bulky precipitate, which soon changes to a heavy granular blood-red powder.

Like the isatinates, the chlorisatinates combine with the sulphurous acid, forming salts of the formula $C_{16} \left\{ \begin{smallmatrix} H^4 \\ Cl \end{smallmatrix} N O_4, 2 S O_2 + M O. \right.$ In short, the analogy between isatine and chlorisatine, isatinates and chlorisatinates, &c., is such as to furnish a very beautiful example of the substitution of chlorine for hydrogen, while the type or chemical character of the compound is unaffected. In bichlorisatine, we shall see an additional example of the same truth.

Bichlorisatine, $C_{16} \left\{ \begin{smallmatrix} H^3 \\ Cl_2 \end{smallmatrix} N O_4, \right.$ is formed along with the preceding compound. It is more soluble than chlorisatine, but is otherwise remarkably similar to it. With aqua potassæ it first forms a deep red solution (here, as in the case of isatine and chlorisatine, a compound of it with potash), which, when heated, changes to yellow, and on evaporation yields yellow scales of a salt composed of potash and bichlorisatinic acid. The acid may be separated by stronger acids as a yellow powder, which, when dissolved and warmed, is resolved into bichlorisatine and water.

Its formula is $C_{16} \left\{ \begin{smallmatrix} H^4 \\ Cl_2 \end{smallmatrix} N O_4, H O. \right.$ The salt of baryta, $C_{16} \left\{ \begin{smallmatrix} H^4 \\ Cl_2 \end{smallmatrix} N O_4, Ba O, \right.$ forms golden-yellow needles. The salt of copper is at first bulky and brown, but soon becomes greenish-yellow and crystalline, and finally, a heavy granular powder of a fine carmine red color.

Bichlorisatine with sulphites forms compounds analogous to those above mentioned of isatine and chlorisatine. In this case also, therefore, the type is perfectly retained, although 2 eq. of the hydrogen of isatine have been replaced by chlorine.

Bromine acts on isatine, and forms two compounds, bromisatine and bibromisatine, entirely analogous to chlorisatine and bichlorisatine, forming bromisatinic and bibromisatinic acids, and also compounds with sulphites analogous to those just mentioned. We have, therefore, from isatine and isatinic acid, by substitution, the following compounds :

Isatine	C_{16}	$H^5 N O_4$
Isatinic acid	C_{16}	$H^6 N O_5 + H O$
Chlorisatine	C_{16}	$\left\{ \begin{smallmatrix} H^4 \\ Cl \end{smallmatrix} N O_4 \right.$
Chlorisatinic acid	C_{16}	$\left\{ \begin{smallmatrix} H^5 \\ Cl \end{smallmatrix} N O_5 + H O \right.$
Bichlorisatine	C_{16}	$\left\{ \begin{smallmatrix} H^3 \\ Cl_2 \end{smallmatrix} N O_4 \right.$
Bichlorisatinic acid	C_{16}	$\left\{ \begin{smallmatrix} H^4 \\ Cl_2 \end{smallmatrix} N O_5 + H O \right.$
Bromisatine	C_{16}	$\left\{ \begin{smallmatrix} H^4 \\ Br \end{smallmatrix} N O_4 \right.$
Bromisatinic acid	C_{16}	$\left\{ \begin{smallmatrix} H^5 \\ Br \end{smallmatrix} N O_5 + H O \right.$

Bibromisatine . . .	C ₁₆	$\left\{ \begin{array}{l} \text{H}_3 \\ \text{Br}_2 \end{array} \right. \text{N O}_4$
Bibromisatinic acid .	C ₁₆	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Br}_2 \end{array} \right. \text{N O}_5 + \text{H O}$
Isatinosulphites . .	C ₁₆	$\left\{ \begin{array}{l} \text{H}_3 \\ \text{Br}_2 \end{array} \right. \text{N O}_4, 2 \text{S O}_2 + \text{M O}$
Chlorisatinosulphites	C ₁₆	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Cl} \end{array} \right. \text{N O}_4, 2 \text{S O}_2 + \text{M O}$
Bichlorisatinosulphites	C ₁₆	$\left\{ \begin{array}{l} \text{H}_3 \\ \text{Cl}_2 \end{array} \right. \text{N O}_4, 2 \text{S O}_2 + \text{M O}$
Bromisatinosulphites	C ₁₆	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Br} \end{array} \right. \text{N O}_4, 2 \text{S O}_2 + \text{M O}$
Bibromisatinosulphites	C ₁₆	$\left\{ \begin{array}{l} \text{H}_3 \\ \text{Br}_2 \end{array} \right. \text{N O}_4, 2 \text{S O}_2 + \text{M O}.$

Hoffman has lately shown that isatine when heated with potash, yields aniline, (see aniline), and that chlorisatine, bromisatine, &c., when treated in the same way, yield compounds of the type of aniline, in which hydrogen is replaced by chlorine, bromine, or both. Some of these compounds retain the basic character, and are therefore very interesting, as the first examples of such chlorinized or brominized bases. A table of the compounds derived by substitution from aniline is given under that substance. Here we have only space to mention that chloraniline, dichloraniline, bromaniline, and dibromaniline, are crystalline volatile bases, forming crystallizable salts, and very analogous to aniline: while in trichloraniline, tribromaniline, chlorodibromaniline, the basic character is lost.

Isatyde, C₁₆ H₅ N O₄ = C₁₆ H₅ N O₄, H, is formed when an alcoholic solution of isatine is acted on by sulphide of ammonium. It is a gray crystalline powder, and may be considered to represent isatine plus 1 eq. hydrogen.

Sulphésatyde, C₁₆ H₅ N $\left\{ \begin{array}{l} \text{O}_2 \\ \text{S}_2 \end{array} \right.$ is isatyde, in which 2 eq. oxygen are replaced by sulphur. It is formed by the action of sulphuretted hydrogen on isatine dissolved in alcohol, and is a grayish-yellow amorphous powder. Sulphisatine is the name of a compound obtained in the same way by Erdmann, which he considers to be different from sulphésatyde.

Chlorisatyde, C₁₆ $\left\{ \begin{array}{l} \text{H}_3 \\ \text{Cl} \end{array} \right. \text{N O}_4$, is a white powder somewhat crystalline, obtained by the action of sulphide of ammonium on chlorisatine. It is perfectly analogous to isatyde. By the action of sulphuretted hydrogen on chlorisatine, a compound is formed which is C₁₆ $\left\{ \begin{array}{l} \text{H}_3 \\ \text{Cl} \end{array} \right. \text{N S}_4$; that is chlorisatyde, in which all the oxygen is replaced by sulphur.

Bichlorisatyde, C₁₆ $\left\{ \begin{array}{l} \text{H}_4 \\ \text{Cl}_2 \end{array} \right. \text{N O}_4$, and bibromisatyde, C₁₆ $\left\{ \begin{array}{l} \text{H}_4 \\ \text{Br}_2 \end{array} \right. \text{N O}_4$, are perfectly analogous, in formation and properties, to chlorisatyde.

Sulphasatyde, $C_{16}H_6N \left\{ \begin{smallmatrix} O_2 \\ S \end{smallmatrix} \right.$ is formed by the action of potash on sulphésatyde, from which it differs in having only 1 eq. oxygen replaced by sulphur. It is a white crystalline powder.

Indine, $C_{16}H_6NO_2$ is a crystallized substance of a beautiful rose color, formed by the action of potash on sulphésatyde, along with the preceding; or by the action of potash on sulphasatyde or isatyde. In the last case isatinate of potash is also formed: thus, $3(C_{16}H_6NO_4) + 2KO = 2(KO, C_{16}H_6NO_2) + C_{16}H_6NO_2$. It is sulphésatyde, minus 2 eq. sulphur, and is also isomeric with white indigo. It is decomposed by nitric acid and by bromine, which give rise to new products.

When indine, moistened with alcohol, is covered with a lukewarm solution of potash, it forms a black solution which in a few moments becomes a semi-solid mass of black needles, which are a compound of potash with indine, or rather with indinic acid, an acid formed from indine, like isatinic acid from isatine, by the assimilation of 1 eq. water, and which is very easily again resolved into indine and water.

Hydrindine is a yellow crystalline compound formed by heating indine, sulphasatyde, or isatyde with potash. Its composition is $C_{22}H_{13}N_2O_5$, that is, 2 eq. indine plus 1 eq. water; and when strongly heated, it is resolved into indine and water. It is not composed of these substances, however, for it forms with potash a white salt, hydrindinate of potash. The acid in this salt appears to be formed, like some of those already described, by the addition of water to hydrindine; its formula is probably $C_{16}H_{13}N_2O_7, 2H_2O$.

Nitrindine, $C_{16}H_4N_2O_7$, is a beautiful violet-colored powder formed by the action of nitric acid on indine and hydrindine. It is indine, in which 2 eq. hydrogen are replaced, one by oxygen

the other by nitrous acid, $C_{16} \left\{ \begin{smallmatrix} H_4 \\ NO_4 \\ O \end{smallmatrix} \right\} NO_2$.

Chlorindine, $C_{16} \left\{ \begin{smallmatrix} H_5 \\ Cl \end{smallmatrix} \right. NO_2 + 2H_2O$, is a powder of a dirty violet color, formed by the action of heat on chlorisatyde. Analogous compounds are obtained from bichlorisatyde and bibromisatyde. Bichlorindine is like chlorindine. Bibromindine is very dark red, and dissolves in alcohol with a fine purple color.

The action of potash on isatyde appears to be the type of its action on chlorisatyde, bromisatyde, bichlorisatyde, and bibromisatyde. When isatyde is acted upon by potash, it yields isatine (or isatinate of potash); indine (or indinate of potash); and hydrindine (or hydrindinate of potash). 6 eq. isatyde, ($6C_{16}H_6NO_4$) are equal to 4 eq. isatine ($4C_{16}H_5NO_4$) + 2 eq. indine ($2C_{16}H_6NO_2$) + 4 eq. water: or they are equal to 4 eq. isatine ($4C_{16}H_5NO_4$) + 1 eq. hydrindine ($C_{22}H_{13}N_2O_5$) + 3 eq. water. Both changes prob-

ably occur, and the three compounds, isatine, indine, and hydrindine, alike take up the elements of water to form the acids, which, to avoid confusion, are not here expressed. Now there is good reason to believe that precisely analogous changes occur when potash acts on bichlorisatyde and on bibromisatyde, each yielding three corresponding compounds, and three acids derived from these. The reader, by strictly following the analogy of the formulæ given above for the action of potash on isatyde, will easily be able to construct the equations for the other analogous cases.

When sulphésatyde is acted on by bisulphite of ammonia, there is formed, among other products not fully investigated, a salt formed of ammonia united to a new acid, sulphisatanous acid, quite different from the acid in the salts formed when isatine is acted on by sulphites. This new acid is $C_{16}H_8N O_3, 2SO_2 + H O$, or perhaps rather, $C_{16}H_8N \left\{ \begin{smallmatrix} O_2 \\ 2SO_2 \end{smallmatrix} \right\} + H O$; that is, sulphésatyde, in which the 2 eq. of sulphur have been replaced by 2 eq. sulphurous acid.

The action of bisulphite of ammonia on sulphésatyde sometimes gives rise to the formation of different products: among others, to an insoluble white powder, isatan, $C_{16}H_8N O_3$, which when heated yields isatine and indine, $3(C_{16}H_8N O_3) = C_{16}H_8N O_4 + 2(C_{16}H_8N O_2) + H O$. Both indine and nitrindine, when acted on by bisulphite of ammonia, appear to produce compounds analogous to those derived from sulphésatyde.

Chlorindopten is the name given by Erdmann to a volatile crystalline substance, formed along with the chlorisatine and bichlorisatine, when chlorine acts on indigo. When the chlorinized mass is distilled with water, this substance passes over in white crystals, which are acid, and evidently a mixture of two substances. When this chlorindopten is heated with potash, a neutral substance passes over, in white crystals similar to the original ones; this is chlorindatmit; while the potash retains an acid of a disagreeable odor, chlorindoptenic acid.

Chlorindoptenic acid, $C_{12}H_4Cl_3 O, H O$, is separated from its potash salt by acids, as a white flocculent matter of a very disagreeable odor. Laurent has identified it with his chlorophenismic acid, an acid derived from coal-tar by the action of chlorine, and makes its formula $C_{12} \left\{ \begin{smallmatrix} H_2 \\ Cl_3 \end{smallmatrix} \right\} O, H O$. Chlorindatmit appears to be trichloraniline, $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Cl_3 \end{smallmatrix} \right\} N$. — (*Hoffmann*).

By the farther action of chlorine on chlorisatine or bichlorisatine, dissolved in alcohol, new compounds are formed, among which are chlorinized chlorindopten, which, like chlorindopten, is a mixture apparently of chlorindatmit, with an acid, chlorinized chlorindoptenic acid, $C_{12}Cl_5 O, H O$; which is the chlorophenusic acid of Laurent. This acid is accompanied by chloranile, $C_{12}Cl_4 O_4$,

a neutral body in volatile golden yellow scales, soluble in hot alcohol, which is also derived from the oil of coal-tar, or rather from the hydrate of phenyle or carbolic acid of that oil, from which chlorophenisic and chlorophenusic acids are obtained.

Chloranile dissolves in weak potash with a deep purple color, and the solution deposits dark purplish-red crystals, composed of potash and a new acid, chloranilic acid. This acid forms scarlet or yellow crystals, according as it contains water of crystallization or not. Its formula is $C_{12}Cl_2O_6, 2H_2O$, or C_6ClO_3, H_2O .

When chloranile is acted on by aqua ammoniæ, it is dissolved, forming a blood-red solution, which deposits chesnut-brown crystals of chloranilammon, $C_6H_3HClO_3 + 4aq. = C_6ClO_3 + NH_3 + 4aq.$ It dissolves in water with a purple color, and when a saturated solution is mixed with hydrochloric acid, it deposits very brilliant black needles of great length. These are a new compound, chloranilam, $C_{12}Cl_2H_3NO_6 = C_{12}Cl_2O_6 + NH_3$; that is, 2 eq. of chloranilammon, $2(C_6ClO_3, NH_3) = C_{12}Cl_2O_6, N_2H_6$, minus 1 eq. ammonia NH_3 . Both these compounds give precipitates with metallic solutions, which are the same from both, but distinct from those formed by chloranilic acid or its salts. Chloranilammon, according to Laurent, is the ammonia salt of an acid containing amide as an ingredient. Chloranilam is the acid itself.

By the action of ammonia on isatine there are produced several new compounds, varying with the strength of the ammonia, and the menstruum employed. In these compounds, oxygen is replaced by amide, NH_2 , or imide, $\frac{1}{2}NH = Im$.

Imesatine is formed when dry ammonia is passed through an alcoholic solution of isatine. It forms fine deep yellow crystals, the formula of which is $C_{16}H_5N_2O_2 = C_{16}H_5N \begin{Bmatrix} O_2 \\ Im_2 \end{Bmatrix}$.

Imasatine is formed when aqua ammoniæ acts on a solution of isatine in alcohol. It is a grayish-yellow crystalline substance, the formula of which is $C_{16}H_5N \begin{Bmatrix} O_2 \\ Im \end{Bmatrix} ?$

Imasatinic acid is formed along with the preceding, and is dissolved along with ammonia. By the addition of an acid it is precipitated as a beautiful scarlet crystalline powder, soluble in hot alcohol, which deposits it in splendid tabular crystals similar to the sublimed periodide of mercury. It dissolves sparingly in acids with a violet color, and these solutions deposit violet crystals. Its formula is $C_{16}H_5N \begin{Bmatrix} O_2 \\ Im \end{Bmatrix} + H_2O$.

Amasatine is formed along with the two preceding bodies. It has a fine yellow color, and dissolves in acids with a violet color, apparently passing into imasatinic acid. Its formula is $C_{16}H_5N \begin{Bmatrix} O_2 \\ Ad \end{Bmatrix} + H_2O$ ($Ad = NH_2 = \text{amide}$).

The analogy between chlorisatine, &c., and isatine, holds in regard to the action of ammonia on them. By the action of dry ammonia on an alcoholic solution of chlorisatine there is formed a yellow crystalline compound, analogous to imesatine. It is called imechlorisatinase, and its formula is $C_{16} \left\{ \begin{array}{c} H_4 \\ Cl \end{array} \right\} N \left\{ \begin{array}{c} O_2 \\ 2HN. \end{array} \right\}$

Imachlorisatinase is analogous to imasatine. Its formula is $C_{16} \left\{ \begin{array}{c} H_4 \\ Cl \end{array} \right\} N \left\{ \begin{array}{c} O_2 \\ NH. \end{array} \right\}$. It forms brownish-yellow crystals.

Imabromisatinase, formed by the action of dry ammonia on dibromisatine in alcohol, is $C_{16} \left\{ \begin{array}{c} H_2 \\ Br_2 \end{array} \right\} N \left\{ \begin{array}{c} O_2 \\ NH. \end{array} \right\}$. It is a deep orange crystalline powder.

We have now briefly run over the catalogue of the very remarkable compounds derived from indigo by the action of sulphuric acid and bichromate of potash, which produces isatine, and by the action of chlorine either on indigo or on isatine, of bromine on the same, and of potash, ammonia, sulphuretted hydrogen and sulphide of ammonium on the products of these actions. The nomenclature of these compounds is in a very imperfect state, and requires reformation, but this cannot be effected until the substances themselves have been more thoroughly studied. It is most important to observe, that by or through chloranile and the chlorindoptenic acids, the series to which indigo belongs connects itself with that of carbolic acid or hydrate of phenyle, (to be afterward described), and these again with the series of salicyle. We have now to mention one or two products of the action of nitric acid on indigo which are common to all these series, and like chloranile, seem likely to be very frequently met with as products of the decomposition of organic compounds.

Anilic Acid. SYN. *Indigotic Acid*; *Nitrosalicylic Acid*, $C_{14}H_4N O_5$, $H O$.—This acid is formed by the long-continued action of weak nitric acid on indigo. It is also formed in the preparation of isatine, if the action be pushed too far. It is identical with nitrosalicylic acid, obtained by the action of nitric acid on salicylic acid or on salicine. It forms fine yellowish-white prisms, which are light and bulky, and shrink much in drying. It is fusible and volatile. By the action of strong nitric acid it is converted into oxalic and picric acids. It requires 1000 parts of cold water for solution. Its salts crystallize well, and their general formula is $C_{14}H_4N O_5, M O$. The anilate of oxide of methyle is obtained as a crystalline compound by the moderated action of nitric acid on the salicylate of oxide of methyle (oil of gaultheria). The anilate of oxide of ethyle is exactly similar.

Picric Acid. SYN. *Carbazotic Acid*; *Nitropicric Acid*; *Nitrophenic Acid*, $C_{12} \left\{ \begin{array}{c} H_2 \\ 3NO_4 \end{array} \right\} O, H O$.—This acid is formed by

the action of nitric acid on anilic acid, indigo, salicine, salicylic acid, hydrate of phenyle or carbolic acid, coumarine, silk, aloes (!), and other substances. It is most easily formed from carbolic acid, salicine, or oil of gaultheria, by the action of an excess of fuming nitric acid assisted by heat. It is purified by solution in hot water and recrystallization. It forms pale yellow or even white scales of a silvery lustre. They dissolve in hot water with a strong yellow color, and a very bitter taste. The acid is fusible and volatile. Its salts crystallize most readily, and all explode when heated. When these salts are put in contact with lime and green vitriol, blood-red solutions are formed, containing the lime salt of a new acid. The picrate of potash is so sparingly soluble, especially in alcohol, that an alcoholic solution of picric acid may be used as a test for potash.

Picric acid is interesting as occurring among the products of the decomposition by nitric acid of so many different substances. It is easily derived from the series of phenyle, that is, from carbolic acid, $C_{12}H_5O, H_2O$. Derived from this we have chlorophenesic acid, $C_{12} \left\{ \begin{smallmatrix} H_2 \\ Cl_2 \end{smallmatrix} \right\} O, H_2O$, chlorophenusic acid, $C_{12}Cl_2O, H_2O$, and picric acid, $C_{12} \left\{ \begin{smallmatrix} H_2 \\ 3NO_2 \end{smallmatrix} \right\} O, H_2O$. It is, therefore, carbolic acid, in which 3 eq. of hydrogen are replaced by 3 eq. of nitrous acid.

When indigo is heated with concentrated potash, there are formed two new acids: chrysanic acid, the composition of which is uncertain, and anthranilic acid, $C_{14}H_7NO_4 = C_{14}H_5NO_2, H_2O$. The latter is purified in the form of anthranilate of potash, and the acid separated by an excess of acetic acid. It forms transparent yellow scales, which, however, when quite pure, are colorless. It is derived from blue indigo, $C_{16}H_5NO_2$, by the loss of 2 eq. carbon, and the addition of 2 eq. water.

When anthranilic acid is mixed with powdered glass, and rapidly heated, it is resolved into carbonic acid, and an oily liquid which is aniline, a very powerful base, devoid of oxygen, identical with the crystalline of Unverdorben, and the kyanol of Runge, $C_{12}H_7N$. This metamorphosis is very simple: $C_{14}H_7NO_4 = 2CO_2 + C_{12}H_7N$. Since aniline is obtained in many other cases of decomposition of organic matters by heat, it becomes a substance of great interest.

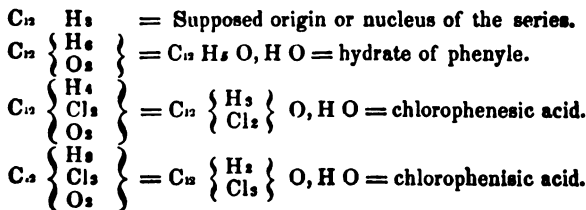
Aniline is recognized by its property of striking a deep violet-blue color with chloride of lime. It obtained the name kyanol from this property. Its other name, crystalline, indicates its great tendency to form crystallizable salts with acids.

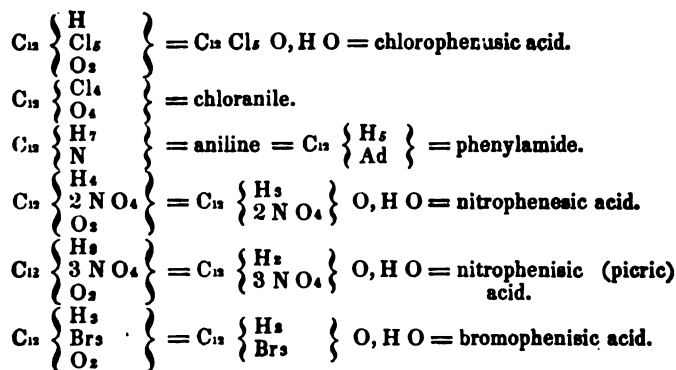
The recent researches of A. W. Hoffman have greatly extended our knowledge of this remarkable compound. He has shown that it is best obtained by heating isatine with potash, thus $C_{12}NH_2$

$O_4 + 4(KO, H O) = C_{11}H_7N + 4(KO, CO_2) + H_2$. But he has also proved that its formation is not confined to the products of the decomposition of indigo, it being formed when other substances, isomeric with anthranilic acid, are exposed to heat along with bases, such as lime or baryta. Such substances are salicylamide and protonitrobenzoëne or nitrotoluide, both of which have the empirical formula, $C_{11}H_7NO_4$. The former yields little, but the latter is entirely resolved into aniline and carbonic acid. He has also fully identified aniline with the crystalline of Unverdorben, a base occurring with others among the products of distillation of animal matter, and in coal-tar. It is worthy of remark, that a close connection may be traced between aniline and carbohic acid, (hydrate of phenyle). The latter is $C_{12}H_5O, HO$. The carbolate of ammonia, $C_{12}H_5O, NH_4O$, minus 2 eq. water, would yield an amide, phenylamide, which would be $C_{12}H_5NH_2 = C_{12}H_7N$; and this is aniline. Now, in Hoffman's experiment, above mentioned, in which salicylamide was heated with lime, it did not yield much aniline, but on the other hand, it furnished a large quantity of carbohic acid.

It is further to be noticed that carbohic acid (hydrate of phenyle) and aniline (phenylamide) occur together in coal-tar; and that all the substances which yield either one or other of these are also converted into picric acid, $C_{12} \left\{ \begin{smallmatrix} H_3 \\ 3NO_4 \end{smallmatrix} \right\} O, HO$, by the action of nitric acid. Thus carbohic acid, indigo, salicine, and salicylic acid are all transformed into picric acid, by excess of nitric acid.

Another point in which all these substances agree is this, that when acted on by a mixture of hydrochloric acid and chlorate of potash, they are all converted into chloranile, $C_{12}Cl_4O_4$. It is more than probable that all those bodies, such as indigo, salicine, carbohic acid, &c., which in this way yield chloranile, either belong to the series of phenyle or are nearly allied to that series, and readily pass into it. The fundamental or primitive compound of that series appears to be some compound of the formula, $C_{12}\Delta$, where Δ stands for hydrogen, chlorine, bromine, iodine, oxygen, nitrous acid, &c. Assuming this, and supposing Δ to be represented by H, then we have the following series, which will exhibit in a practical form the doctrine of substitutions.





Hoffman has shown that isatine, when distilled with potash, yields aniline; and that chlorisatine, so analogous in all respects to isatine, undergoes a similar decomposition, yielding a new base, chloraniline; also that other compounds may be formed containing more chlorine, but still belonging to the same series; that bromisatine also yields a base, bromaniline; finally that by the action of ammonia and sulphuretted hydrogen on binitrobenzide or dinitrobenzole, there is formed a base, nitraniline, in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid, and that in this base 2 eq. of hydrogen may farther be replaced by bromine, yielding a neutral body. The following are the formulæ of these new compounds, which, it will be observed, are still referable to the original formula, $\text{C}_{12} \Delta^5$ or $\text{C}_{12} \text{H}_5$.

Aniline	C_{12}	H_7	N	basic. Amaphenase.
Chloraniline	C_{12}	$\left\{ \begin{array}{l} \text{H}_5 \\ \text{Cl} \end{array} \right\}$	N	basic. Amachlophenese.
Dichloraniline . . .	C_{12}	$\left\{ \begin{array}{l} \text{H}_5 \\ \text{Cl}_2 \end{array} \right\}$	N	basic. Amachlophenise.
Trichloraniline . . .	C_{12}	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Cl}_3 \end{array} \right\}$	N	neutral. Amachlophenose.
Bromaniline	C_{12}	$\left\{ \begin{array}{l} \text{H}_5 \\ \text{Br} \end{array} \right\}$	N	basic. Amabrophenese.
Dibromaniline . . .	C_{12}	$\left\{ \begin{array}{l} \text{H}_5 \\ \text{Br}_2 \end{array} \right\}$	N	basic. Amabrophenise.
Tribromaniline . . .	C_{12}	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Br}_3 \end{array} \right\}$	N	neutral. Amabrophenose.
Chlorodibromaniline	C_{12}	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Cl} \\ \text{Br}_2 \end{array} \right\}$	N	neutral. Amachlobrophenose.
Nitraniline	C_{12}	$\left\{ \begin{array}{l} \text{H}_5 \\ \text{N O}_4 \end{array} \right\}$	N	basic. Amanitrophenese.
Nitrodibromaniline	C_{12}	$\left\{ \begin{array}{l} \text{H}_4 \\ \text{Br}_2 \\ \text{N O}_4 \end{array} \right\}$	N	neutral. Amanitrobrophenose.

It may here be mentioned, that although, in order to include the water of the hydrated acids, I have adopted $C_{12}H_5$ as the nucleus of these compounds, we may also refer them to $C_{12}H_6$ = phène or benzine. The oxide of phenyle and the different acids will then be represented as anhydrous, thus, $C_{12} \left\{ \begin{smallmatrix} H_5 \\ O \end{smallmatrix} \right.$ oxide of phenyle, &c. Aniline will be $C_{12} \left\{ \begin{smallmatrix} H_5 \\ N H_2 \end{smallmatrix} \right.$ = $C_{12} \left\{ \begin{smallmatrix} H_5 \\ Ad \end{smallmatrix} \right.$ = phenylamide; and chloraniline will be $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Cl \\ Ad \end{smallmatrix} \right.$ and so on. The only compound which does not adapt itself to this formula, is chloranile, $C_{12} Cl_4 O_4$; which might, however, be $C_{12} \left\{ \begin{smallmatrix} Cl_3 \\ O_2 \text{ or } Cl O_2 \end{smallmatrix} \right.$ or $C_{12} \left\{ \begin{smallmatrix} Cl_2 \\ 2 Cl O \end{smallmatrix} \right.$

Our space will not permit us to enter into any details concerning the preparation and properties of these interesting compounds; but it may be remarked that chloraniline by the action of hydrochloric acid and chlorate of potash yields chloranile; and that the same substance, when passed over lime (hydrated?) at a low red-heat, yields aniline, thus affording additional proof that all these compounds belong to one series, and are different subtypes of one general type. Nor must it be forgotten that in the case of aniline, chloraniline, and bromaniline, we have chlorine and bromine substituted for hydrogen in a basic compound, without affecting its basic characters. This is the first known example of a base formed by substitution from another base, although similar facts, in regard to acids and neutral bodies, had long been known.

It is very well worthy of remark that a certain amount of chlorine or bromine, usually so antagonistic to hydrogen, does not, when substituted for that element, destroy the basic character; but that the chlorine and bromine appear to assume the function of hydrogen. A large proportion, however, of these elements, does efface the basic character.

But the existence of nitraniline is even more remarkable. In this body, 1 eq. of hydrogen in aniline has been replaced by 1 eq. of a powerful acid, nitrous acid, and yet the compound is decidedly basic, and retains the type of aniline.

Nitraniline forms fine golden-yellow prisms, and with acids yields crystallizable salts. When acted on by bromine, it yields nitrodibromaniline, a neutral compound in which 2 more eq. of hydrogen are removed and replaced by bromine.

We have here considered aniline chiefly in reference to its derivation from indigo and isatine, and the other derived bases of the same type, as also connected with indigo through chlorisatine, &c. Under the head of organic bases, a few pages

farther on, we shall describe more particularly the properties of aniline, and some others of its derivatives.

13. CARMINE.

This name has been given to the coloring matter of cochineal which is nitrogenized, and may be obtained in dark red crystalline grains, very soluble in water and alcohol. It forms with alumina a beautiful red lake, well known as carmine. Its precise formula is not determined, but it approaches to $C_{22}H_{12}N_2O_{10}$.

Preisser states that the red coloring matter, like all vegetable colors, is derived by oxidation from a colorless crystalline compound which he calls carmine. To the red compound he gives the name of carmine. He has analyzed neither. It may here be mentioned that Preisser has succeeded in isolating the colorless compounds (from which, as he states, the colors are derived by oxidation, especially with the aid of ammonia) in most of the red and yellow dye stuffs, such as Brazilwood, safflower, sandalwood, quercitron, woad, annotta, fustic, &c. He obtains them by forming lakes of the colors with oxide of lead, decomposing the lakes by sulphuretted hydrogen, which deoxidizes the coloring matter, when the colorless basis is dissolved, and obtained in crystals by evaporating rapidly, or in vacuo, to avoid oxidation. He has analyzed some of these compounds, but his results are not yet complete.

The finest crimson and scarlet dyes are made from cochineal, according as the mordant is alumina and tin.

Kermes is a dye stuff similar in its origin and properties to cochineal, but inferior in beauty of tint. It is derived from *coccus ilicis*.

The red coloring matter of stick-lac, which is also used as a dye, has similar properties. Lac is produced on certain plants by the puncture of an insect.

ACTION OF NITRIC ACID ON ALOES.

This action so much resembles, in some points the action of nitric acid on indigo, that it may be properly mentioned here. Aloes is the well known inspissated juice of certain species of aloe, and is very bitter and purgative. The nature of its active principle is still unknown: but when heated with nitric acid it yields a yellow bitter substance, which is converted, by the farther action of the acid, into two crystallizable acids, chrysammic and chrysolepic acid. The artificial bitter of aloes appears to be formed of two acids, aloetic and aloeretic acids, which form red salts, but the composition of which is not exactly ascertained.

Chrysammic acid, $C_{15}H_8N_2O_{12}$, H_2O , is obtained as a yellow precipitate, when water is added to the solution obtained by heating aloes with excess of nitric acid. It is purified by being combined with potash, and this salt, after recrystallization, is dissolved.

in hot water and decomposed by diluted nitric acid. The chrysammic acid is deposited as a powder formed of golden-yellow shining scales. Its solution is of a fine purple. All its salts are crystallizable and of a deep red color, frequently with green reflection, like murexide. The chrysammate of ammonia forms dark green crystals, which, when dissolved and acted on by nitric acid, deposit brilliant black scales, which are not chrysammic acid, but are transformed into it when boiled with acids or bases. The solution of chrysammate of ammonia gives with metallic salts peculiar precipitates distinct from those formed with the same salts by chrysammate of potash.

Chrysolepic acid, $C_{11}H_2N_2O_5$, $H O$, has the formula and many of the properties of picric acid; but is said by Schunk, who discovered it, to be different. It is darker in color, and its salt with potash is much more soluble than picrate of potash. It would, however, appear that the two acids are essentially the same; for their salts are in general very similar, and all explode when heated. Now that picric acid is recognized as so frequent a product of the action of nitric acid, we have no difficulty in understanding its occurrence here.

ALCALOIDS OR ORGANIC BASES.

These names are given to a class of nitrogenized organic compounds which, in their relations, are quite analogous to ammonia, or rather to oxide of ammonium. They are to be distinguished from such basic oxides as oxide of ethyle, oxide of methyle, &c., which contain no nitrogen, and, although they form neutral compounds with acids, yet exist in a peculiar state in these compounds, which cannot be decomposed, like ordinary salts, by double decomposition. Thus, oxalate of oxide of ethyle does not precipitate with nitrate of lime, and chloride of ethyle does not decompose nitrate of silver. But the case is quite different with the alcaloids; for their salts undergo the same decompositions as those of ammonia.

Most of the alcaloids are found in vegetable juices, seeds, or roots; these are called vegetable alcalies, and they are generally the active principles of the plants, for the most part poisonous, in which they are found. But of late, organic bases quite analogous to those produced by nature, have been formed in a variety of processes; as, for example, the singular bases containing platinum, described at pp. 282-287; the bases containing arsenic, or arsenic and platinum, mentioned at pp. 398-402; the bases of coal-tar, of which aniline, formed in several different processes, is one; the bases, chloraniline, &c., derived from aniline; the bases derived from oil of mustard, (see p. 468); those derived from the decomposition of natural alcaloids, as quinoleine and cotarnine; those formed by the action of potash on melam, as melamine and ammelime; those produced by the action of ammonia on oil of bitter

almonds and analogous bodies, such as amarine, lophine, picrine, and furfurine; those formed by the action of sulphide of ammonium on certain nitrogenized bodies, as aniline from nitrobenzide, naphthalidine from nitronaphthalese, thialdine from aldehydammonia, &c.; those derived from kreatine by the action of acids and bases, namely, kreatinine and sarcosine; and such as are formed by the action of acids and bases on other animal compounds, of which glycocoll is an example, being formed from gelatine by the action of potash, and from hippuric acid by the action of hydrochloric acid. Most of these artificially formed bases are of very recent discovery, and it is evident that they must throw much light on the theory of the production of the natural alcaloids, and that the careful study of this part of the subject will, in all probability, eventually lead to the artificial formation of the natural organic bases.

The alcaloids possess, for the most part, very decided basic properties; when dissolved they act on vegetable colors like the inorganic alcalies; and they neutralize the strongest acids completely, generally forming crystallizable salts. Most of them, at the ordinary temperature, are expelled from their salts by ammonia, but many of them at the heat of boiling water expel ammonia from its salts, owing to the volatility of the latter alkali.

Their basic properties are not derived from the oxygen they contain, for no variation in the amount of that element affects their neutralizing power. On the other hand, there is every reason to believe that their basic character depends on the nitrogen they contain; for they all, without exception, contain nitrogen, although several are devoid of oxygen. Moreover, most, if not all of those which have been formed artificially, are prepared with the aid of ammonia, or some compound of ammonia, or amidogen. It is quite conceivable that they may be composed of ammonia or amidogen, plus some compound of carbon and hydrogen, or of carbon, hydrogen, and oxygen, the addition of which does not diminish the basic energy of the ammonia or amidogen. We shall return to this subject, after having described the alcaloids. In the meantime we shall first give an account of the natural alcaloids, and afterward proceed to consider the artificial ones.

1. NATURAL ALCALOIDS OR VEGETABLE BASES.

The alcaloids occur in combination, generally with vegetable acids; and they are separated from these combinations by the same means which are employed in the case of inorganic bases, modified in each case, according as the alcaloid is soluble or insoluble in water and other solvents, fixed or volatile when heated. Thus quinine, morphia, and strychnia, are separated by adding to their soluble salts, lime, ammonia, or magnesia, which form soluble salts with the acids which are present, while the alcaloids, being

insoluble, are precipitated; codeine, being soluble in ether as well as water, is first set free by potash, and ether being added to the aqueous liquid, is agitated with it, and rises to the surface, carrying the codeine along with it, and the same process applies to other alcaloids. Lastly, conia, nicotine, and other volatile alcaloids are obtained by distilling their salts with an excess of liquor potassæ.

The alcaloids, like ammonia, combine with hydrogen acids forming salts, without the addition of water or its elements being necessary; they also, like ammonia, refuse to combine with anhydrous oxygen acids, requiring 1 eq. of water to form dry salts. Their hydrochlorates, like sal ammoniac, form double salts with the bichlorides of platinum and of mercury.

The salts of most of the alcaloids are precipitated as tannates by infusion of galls.

The alcaloids are generally decomposed by chlorine, bromine, and iodine, forming colored compounds not yet fully investigated. They are also decomposed by nitric acid, some of them with a deep red color.

Some of them, such as quinine, strychnia, &c., when heated with strong caustic potash, yield an oily compound, which is also a base, and is called quinoleine.

We shall now briefly describe the individual alcaloids, dividing them into groups, according to their characters.

a. Liquid Volatile Bases.

Nicotine, $C_{10}H_8N$. — This base is found in tobacco, and is obtained by distilling the concentrated infusion of the leaves along with potash. The distilled liquid, which contains nicotine, water, and ammonia, is neutralized by sulphuric acid and the neutral solution dried up. Alcohol then dissolves the sulphate of nicotine, leaving undissolved the sulphate of ammonia. The pure sulphate, distilled with potash, yields pure nicotine, which appears as an oily, limpid, colorless liquid, having a weak smell of tobacco. Its Sp. G. is 1.048. It is decidedly alkaline, and mixes with water, alcohol, and ether. It is highly poisonous. With acids it forms salts which crystallize with difficulty. The hydrochlorate of nicotine combines with bichloride of platinum, forming a double salt, which yields large, regular, orange-red crystals, of the formula $C_{10}H_8N, HCl + PtCl_2$. It is probable that nicotine, besides being found in the fresh leaves of tobacco, is produced in larger quantity during the fermentation to which the leaves are subjected in the manufacture of tobacco; and there is also reason to believe that it is produced by the action of heat on tobacco, as in smoking, and that, from the comparative simplicity of its formula, it will be found among the products of the distillation of organic compounds containing nitrogen.

Conicine. SYN. *Conia*, $C_{16}H_{15}N$? — This base occurs in the hemlock, *conium maculatum*, and is extracted by a process quite analogous to that above described for nicotine. It is also an oily liquid, boiling at 338° , highly poisonous, and easily decomposed. Its taste and smell are both very acrid and disagreeable, and somewhat analogous to those of nicotine. Its salts are acrid and poisonous, crystallizing with difficulty. As it is the active principle of the conium, conicine, either pure or as a salt, ought to be used instead of the extract or tincture, which are very variable.

The two bases just described are the only natural bases belonging to the strongly marked group of volatile oily bases. But several artificial compounds are known, which belong to this group. These will be described in their proper place, and it will be seen that their analogy to nicotine and conicine is perfect.

b. Bases of Cinchona Bark.

a. Quinine, $C_{20}H_{19}NO_2$. SYN. *Chinine*. — This important alkaloid is found along with cinchonine, in most species of cinchona bark. It predominates in yellow bark, *cinchona flava*, *China regia*, or *China calisaya*; and is obtained by boiling with an excess of milk of lime the decoction in diluted hydrochloric acid of the bark, and treating the precipitate with hot alcohol, which dissolves cinchonine and quinine. On evaporation, the cinchonine is deposited in crystals, and the quinine remains dissolved. Water is added, which causes the quinine to separate as a resinous mass. It may be obtained in crystals by the spontaneous evaporation of its solution in absolute alcohol. It is very sparingly soluble in water, but very soluble in alcohol and in acids. Its solutions are very bitter. When heated with hydrate of potash, it yields carbonate of potash, hydrogen gas, and quinoline or leukoline, (see that substance).

Quinine is decidedly alkaline, and neutralizes the acids. Its salts, especially the sulphate, are very much used in medicine, especially as febrifuge and tonic remedies, in most cases very superior to the bark in substance. The sulphate of quinine used in medicine is a basic salt, $2(C_{20}H_{19}NO_2) + SO_3 + 8H_2O$. The neutral sulphate is much more soluble in water; hence in draughts, sulphate of quinine is generally dissolved in diluted sulphuric acid. The hydrochlorate, phosphate, citrate, and ferrocynate of quinine have also been employed in medicine.

b. Cinchonine, $C_{20}H_{17}NO$. — This base predominates in the gray bark, *cinchona condaminea*, or *C. rubiginosa*, and is also found in large quantity, as well as quinine, in red bark, *C. oblongifolia*. Its preparation has been above described. It crystallizes very readily, and is not so bitter as quinine, although highly febrifuge. When heated, a considerable part is sublimed. When distilled with potash, it yields quinoline. It neutralizes the acids, forming crystallizable salts, which may be substituted for those of quinine.

It is very important to observe that cinchonine only differs from quinine by 1 eq. oxygen; and although hitherto no one has succeeded in converting one into the other, little doubt can be entertained that this will be accomplished in process of time. The fact that both yield quinoline is very interesting.

c. Quinoidine. — This name was given by Sertuerner to a third alcaloid, which he found in the mother liquors of the preceding. It has been shown by Liebig to be nothing else than pure quinine, in the amorphous or uncrystallizable state. The cause of its assuming the amorphous state is not yet known. It is very powerful as a remedy, and is now much used under the name of amorphous quinine.

d. Aricine, C₂₀H₁₂N O₃ ? — This base was found in 1828, in a cinchona bark from Arica, in Peru, and has not since occurred. It is very similar to cinchonine, from which it differs in being soluble in ether. According to the analysis of Pelletier, it contains 1 eq. oxygen more than quinine, and 2 eq. more than cinchonine, so that the three bases may be viewed as oxides of the same radical. Aricine forms salts which are crystallizable, bitter and febrifuge.

Besides the above four, other alcaloids are said to have been found in different species of cinchona; as pitoyine, in the *China pitoya*, chinovine in the *China nova*, another alcaloid in the *China of Oarthagena*, blanquinine in the *China blanca*, which is the bark of *cinchona ovifolia* and *C. macrocarpa*; and cinchovatine in *cinchona ovata*. This last crystallizes well, and forms crystallizable salts. It has been analyzed, and the results lead to the formula C₂₂H₁₂N₂O₄.

c. Bases of the Papaveraceæ.

Morphine, C₁₆H₁₆N O₂. — This alcaloid occurs in opium, which is the inspissated juice of *papaver somniferum*. Perhaps the easiest method of extracting it is the following. The soluble part of opium is extracted by water, and the concentrated infusion is mixed with solution of chloride of calcium, this salt being added in slight excess. On standing, especially if warmed, the mixture deposits a copious brownish-gray precipitate of mixed meconate and sulphate of lime (the morphine being in the opium partly as meconate, partly as sulphate), while hydrochlorate of morphine remains in solution with a very large proportion of dark brown coloring matter. The brown solution is evaporated till, on cooling, the hydrochlorate crystallizes, forming a nearly solid mass, which is subjected to very strong pressure in flannel. A thick, viscid, nearly black mother liquor is thus expressed, which contains all the narcotine and coloring matter. The squeezed mass or cake of hydrochlorate of morphine is of a fawn color. It is redissolved in hot water, filtered if necessary, and recrystallized,

so much water being used, that on cooling a semi-solid mass is obtained. This is again squeezed out, and if the squeezed cake is not quite white, it is only necessary to repeat the operation. A little animal charcoal in the second, or better still in the third, crystallization, assists in removing the last traces of color. The second and third mother liquids, although colored, are not to be thrown away, but should be added to the solution of a fresh portion of opium, so that the small quantity of hydrochlorate which is retained in solution shall not be lost. In crystallizing hydrochlorate of morphine, the liquid should always be acidulated with hydrochloric acid (after the animal charcoal is separated), because in this way very little indeed is retained in solution.

The purified hydrochlorate, which still contains about $\frac{1}{10}$ of codeine, is now dissolved in hot water, and supersaturated with ammonia; on cooling, the morphine is deposited as a snow-white crystalline powder, which may be crystallized by means of hot alcohol. The codeine remains in the mother liquor.

Morphine forms hard transparent brilliant crystals, almost insoluble in water, soluble in hot alcohol, insoluble in ether. It is decidedly alkaline, neutralizing acids, and forming crystallizable salts. All its solutions are bitter, and act as narcotic poisons. It is colored red by nitric acid, and brownish-red by iodic acid; it also strikes a deep blue with perchloride of iron.

The salts of morphine are much used in medicine, especially the hydrochlorate, the acetate, and the sulphate. A solution of any of these salts, of five grains to the ounce, may be administered in the same dose as tincture of opium (laudanum). The hydrochlorate or muriate is prepared as above described, and is used in the state in which it is obtained by repeated crystallization, containing $\frac{1}{10}$ of its weight of a double hydrochlorate of morphine and codeine, which has much the same action. The acetate and sulphate are best made directly by dissolving in acetic and sulphuric acids the precipitated morphine till they are neutralized, and then evaporating. 1 lb. of good opium yields $1\frac{1}{2}$ oz. of hydrochlorate of morphine. These salts are most valuable anodynes, and do not derange the stomach nearly so much as an equivalent dose of laudanum; but they do not act so decidedly in producing sleep as in allaying pain and irritation; at least the sleep they induce does not come on so soon as in the case of laudanum. The patient, however, even when he does not sleep, feels refreshed, almost as if he had slept, and on the whole the preparations of morphine are preferred by the physician, and have, in this country at least, nearly banished the use of laudanum. The black drop contains impure citrate of morphine.

Codeine, $C_{18}H_{19}NO_5$. — This alcaloid is obtained as above described, from the mother liquor of the precipitated morphine, which, being evaporated, deposits the double hydrochlorate of

morphine and codeine. This salt being purified, is acted on by potash, which dissolves the morphine, while the codeine is left as a viscid mass, which soon becomes hard and crystalline. It is purified by solution in ether or in water, both of which solvents leave the morphine, which may be mixed with it, undissolved. The ethereal solution, by spontaneous evaporation, deposits it, especially if a little water be added, in fine anhydrous prisms; the aqueous solution gives large octahedral crystals, which are a hydrate, with 2 eq. of water.

Codeine is a powerful base, forming neutral salts with acids. Its solutions are bitter, and would seem to have an anodyne action on the system. But in certain circumstances they appear to excite intolerable itching of the whole skin. It is therefore possible, that the itching caused in some persons by opium, and by the commercial muriate of morphine, proceeds from codeine.

It is important to observe that, as cinchona bark contains three alkaloids differing only in the proportion of oxygen they contain, so the two principal bases of opium differ only by 1 eq. oxygen. Hitherto, however, it has been found impossible to convert codeine into morphine by oxidation, or morphine into codeine by deoxidation.

Thebaine. — This base also occurs in opium. It is nearly insoluble in water, soluble in alcohol and ether. Its solutions are alkaline, and have an acrid metallic taste. It forms crystallizable salts with acids. According to Kane, its formula is $C_{25}H_{14}NO_3$.

Pseudomorphine, $C_{27}H_{18}NO_{14}$? — This base is occasionally found in opium. It forms shining scales. It is sparingly soluble in water and weak alcohol, insoluble in absolute alcohol and in ether. It is readily dissolved by caustic potash or soda. It is colored blue by perchloride of iron. It forms salts with acids, which are as yet little known.

Narceine, $C_{28}H_{20}NO_{12}$? — This, which is a feeble base, also occurs in opium. It is sparingly soluble in water, soluble in alcohol, insoluble in ether. It melts at 197° . It is colored blue by hydrochloric acid, but not by perchloride of iron. Acids dissolve it, but hardly form definite salts with it. In short, it ought rather to be described as an indifferent substance, were it not that its composition so much resembles that of the alkaloids.

Narcotine, $C_{28}H_{22}NO_{14}$. — This is another weak base, found in opium in larger proportion than any other, except morphine. It may be obtained, either from the mother liquor of muriate of morphine by adding ammonia, or by digesting the insoluble part of opium in diluted acetic acid, and precipitating by ammonia. The impure narcotine is purified by solution in hot alcohol, with the aid of animal charcoal. On cooling, narcotine is deposited in crystals, which are insoluble in water and alkalies, soluble in alcohol, ether, and acids. Its salts are bitter, and crystallize with great difficulty.

The very recent researches of Liebig, Wöhler, and Blyth, have made known a series of products of decomposition derived from narcotine, when acted on by peroxide of manganese and sulphuric acid, and also by bichloride of platinum. These our space will only permit us briefly to mention.

1. *Opianic Acid*, $C_{20}H_8O_{10} = C_{20}H_8O_9, H_2O$.—This acid crystallizes in slender prisms, and forms soluble and crystallizable salts with baryta and the oxides of lead and silver, and with oxide of ethyle. When melted, opianic acid passes into an insoluble state, its composition remaining the same.

2. *Opiammon*, $C_{20}H_{17}NO_8$.—This compound is derived from 2 eq. opianate of ammonia by the loss of 1 eq. ammonia and 4 eq. water. It is a pale yellow powder, which, by boiling with water, is converted into opianic acid and opianate of ammonia.

3. *Xanthopenic Acid*.—When opiammon is acted on by alkalies, it gives off ammonia and yields opianate and xanthopenate of potash. An acid separates the xanthopenic acid as a yellow flocculent precipitate. It forms salts of a fine yellow color, but has not been fully examined. It contains nitrogen.

4. *Opiano-sulphurous Acid*, $C_{20}H_8O_{11}S_2H_2O$, is formed by the action of sulphurous acid on opianic acid, and is produced by the substitution of 2 eq. sulphurous acid for 2 eq. water. It has a bitter taste and forms crystallizable salts.

5. *Sulphopianic Acid*, $C_{20}H_8 \left\{ \begin{matrix} O_7 \\ S_2 \end{matrix} \right\} H_2O$. This acid is formed by the action of sulphuretted hydrogen on opianic acid, and is, in fact, opianic acid, in which 2 eq. oxygen are replaced by 2 eq. sulphur. It is an amorphous yellow powder, which crystallizes from alcohol. Its salts are soon decomposed, yielding sulphides of the metals.

According to Wöhler, opianic acid is $(C_{20}H_8O_7, 2H_2O) + H_2O$; and in the two preceding acids the 2 eq. of water represented within the brackets are replaced by 2 eq. sulphurous acid and 2 eq. sulphuretted hydrogen. Opiammon, on this view, is $(C_{20}H_8O_7, 2H_2O) + C_{20}H_8O_7, NH_3$. He considers it probable that narcotine is a compound analogous to opiammon, and containing opianic acid.

6. *Hemipinic acid*, $C_{10}H_4O_5H_2O$.—This is a product of oxidation of opianic acid. 1 eq. anhydrous opianic acid, $C_{20}H_8O_9$, plus 1 eq. oxygen, is $C_{20}H_8O_{10} = 2(C_{10}H_4O_5)$. The hemipinic acid crystallizes in regular four-sided prisms. It forms insoluble salts with the oxides of lead and silver.

7. *Cotarnine*, $C_{25}H_{15}NO_6$.—This is a base formed along with opianic acid. 1 eq. narcotine, $C_{26}H_{18}NO_{11}$, and 7 eq. oxygen, yield 1 eq. cotarnine, $C_{25}H_{15}NO_6 + 1$ eq. opianic acid $C_{20}H_8O_9 + 1$ eq. carbonic acid, $CO_2 + 3$ eq. water, $3H_2O$.

Cotarnine forms a deep yellow radiated mass, soluble in alcohol and in water. It is bitter and alkaline, and forms

crystallizable double salts with the bichlorides of mercury and platinum.

8. *Humopinic Acid* is a dark brown humus-like acid formed by the action of heat on narcotine. Its composition is not established with certainty, but resembles that of other similar bodies. It contains no nitrogen.

9. *Apophyllic Acid*. — This seems to be a product of decomposition of cotarnine. It forms crystals very like those of apophyllite and equally cleavable. When heated it yields an oily liquid, evidently quinoline. Its composition is not yet known, but it contains nitrogen.

10. *Narcogenine*, $C_{28}H_{19}N O_{10}$, is formed, along with opianic acid, when narcotine is not so far oxidized as to yield cotarnine. 2 eq. narcotine with 5 eq. oxygen yield 2 eq. narcogenine, 1 eq. opianic acid, and 3 eq. water. It forms a crystallizable double salt with bichloride of platinum, but when separated, it is resolved into narcotine and cotarnine. 2 eq. narcogenine with 2 eq. oxygen contain the elements of 1 eq. narcotine, 1 eq. cotarnine, and 1 eq. carbonic acid.

11. *Narcotinic Acid*. — When narcotine is heated with potash it forms a soluble compound which contains an acid, apparently isomeric with narcotine, or differing from it only by 1 or 2 eq. water. When this acid, which is called narcotinic acid, is separated from its salts, it rapidly passes into narcotine, so that it is unknown in a separate form. Its atomic weight seems to be half that of narcotine, so that 1 eq. narcotine probably forms 2 eq. of the acid.

Such is a very brief and imperfect account of the results of the recent researches of Wöhler and of Blyth on narcotine. They are of very great importance as indicating a method which may lead to the discovery of the true constitution of the alkaloids.

Chelidonine, $C_{20}H_{15}N_2 O_8$. — This alkaloid occurs in *chelidonium majus*, along with chelerythrine. It is bitter, insoluble in water, and alkaline, forming crystallizable salts.

h. *Chelerythrine*, found in the same plant, forms a gray powder which excites violent sneezing. With acids it forms red salts, which are narcotic and poisonous.

i. *Glaucine*. — This alkaloid occurs in the leaves and stem of *glaucium luteum*. It may be obtained in pearly scales; its taste is bitter and acid, and it forms salts with acids. Its composition is not yet ascertained.

k. *Glaucopictine* is found in the root of the same plant. It is bitter and forms salts of a bitter and nauseous taste. Its composition is unknown.

d. Alkaloids of the Solanaceæ, the Strychnæ, and other Vegetable Families.

Hyoscyamine. — The base is found in *hyoscyamus niger* and other species of hyoscyamus. Its composition is not yet known.

It is extracted from the seeds by a difficult and tedious process, and may also be obtained, although with much loss, by distillation with potash, like conicine. It is very prone to decomposition when in contact with mineral alkalies. It crystallizes, when pure, in radiated groups of needles, but sometimes forms a viscid amorphous mass. When moist it has a stupefying smell like that of tobacco. It is very poisonous, causing, like conicine, tetanic spasms. It dilates the pupil powerfully. It is fusible and volatile, but is partly decomposed when distilled. It dissolves in water, alcohol, and ether. It neutralizes the acids, forming crystallizable salts which are very poisonous.

Daturine. — This base is obtained from the seeds of *datura stramonium*. It is, in preparation and properties, very analogous to hyoscyamine. It is, however, less soluble in water, and crystallizes in fine brilliant prisms, from its alcoholic solution. It is fusible, volatile, and very poisonous, dilating the pupil. Its salts are crystallizable and very poisonous. Its precise composition is unknown.

Stramonine. — This is another crystalline compound found in stramonium. It is crystallizable, volatile, soluble in alcohol and ether, insoluble in water. Its nature is uncertain and its composition unknown.

Atropine, $C_{17}H_{23}NO_3$? — This alkaloid is the active principle of *atropa belladonna*. It is obtained like daturine, and being equally prone to decomposition, much is always lost. It is sparingly soluble in water and ether, more soluble in alcohol. It crystallizes in white silky prisms, and sometimes forms an amorphous mass like glass. It is very bitter, acrid, and poisonous, dilating the pupil like hyoscyamine and daturine. It is fusible and volatile, and neutralizes acids, forming salts which are bitter, acrid, and poisonous, and which crystallize. These salts, from their very powerful action in permanently dilating the pupil, are very well adapted for medical use, being much more uniform than the extract.

e. Solanine, $C_{24}H_{35}NO_8$? — This alkaloid occurs in many species of *solanum*, as in *S. nigrum*, *S. dulcamara*, and in the potato, *S. tuberosum*. In the latter it is found in large quantity, especially in the shoots, when the tubers have germinated in dark cellars. The shoots are extracted with dilute sulphuric acid, and the solution precipitated while hot by ammonia. The precipitate is purified by solution in alcohol. It forms a crystalline powder, very bitter and acrid, and highly poisonous, but not dilating the pupil. Its salts do not crystallize readily. There is some reason to suspect that the alkaloid of the shoots of potatoes may be distinct from that of the bittersweet, *solanum dulcamara*.

f. Veratrine, $C_{21}H_{33}NO_8$? — This alkaloid is found in *veratrum sabadilla*, *V. album*, &c. It is extracted as atropine is, and is gen-

erally obtained as a crystalline powder, nearly white, very acrid and poisonous, exciting when introduced into the nostril violent and even dangerous sneezing. It is insoluble in water, but very soluble in alcohol, and may be obtained, by the spontaneous evaporation of its alcoholic solution, in prismatic crystals several lines in length. It is colored red both by nitric and sulphuric acid.

Veratrine, in the form of tincture, and still more in that of ointment, (1 drachm, or $\frac{1}{2}$ drachm to 1 oz. of lard), is now much used as an external application in neuralgia and obstinate rheumatic pains. Its effects in many cases are highly beneficial. In making the ointment the veratrine should first be rubbed with a few drops of alcohol to an impalpable powder, and the lard then added. If this be not done, the gritty particles of veratrine in the ointment causes so much irritation when rubbed into the skin as to prevent its use for any length of time. We are indebted chiefly to Dr. Turnbull for our knowledge of the valuable properties of this alkaloid.

g. Sabadilline.—This name has been given by Couerbe to a second crystalline body found by him along with veratrine. It is alkaline, soluble in hot water, insoluble in ether, and forms crystallizable salts with acids. Couerbe states its formula to be $C_{26}H_{25}NO_5$; but, according to Simon, it is a compound of veratrine with resin, containing also resinates of soda.

h. Colchicine.—This alkaloid is similar to veratrine, for which it was formerly taken. It is found in *colchicum autumnale*. It is crystallizable, bitter, and very poisonous. Nitric acid colors it blue or violet. It is soluble in water, alcohol, and ether. Its salts are crystallizable, bitter, acrid, and poisonous. They might probably be used in medicine advantageously, instead of the very uncertain preparations of colchicum which are at present employed. In a very small dose, colchicine causes purging and vomiting. Its composition is unknown.

i. Aconitine.—This alkaloid, the composition of which is unknown, is found in *aconitum napellus*, and, probably, also in *A. ferox* and other species. It is obtained by the usual method, but, being very prone to suffer change, much is lost. It forms a crystalline powder, or occasionally a vitreous amorphous mass. It is in the highest degree bitter, acrid, and poisonous, and is said by Geiger to dilate the pupil. On the other hand, the plant contracts the pupil and causes numbness of the part to which it is applied, and Dr. Turnbull has obtained an aconitine possessing these properties in a very high degree. Either, therefore, there are two bases in the aconite, or, as is much more probable, the aconitine of Geiger having an action different from that of the plant, is a product of decomposition, while that of Turnbull is unchanged.

Turnbull's aconitine is an invaluable remedy in the same painful diseases in which veratrine is employed. It is unfortunately

obtained in small proportion, and as yet is very expensive. A cheaper and more productive method of preparing it is a very great desideratum.

k. Delphine, $C_{27}H_{19}NO_2$? — This alcaloid, analogous to veratrine, found in *stavesacre*, *delphinium staphysagria*. It has only been obtained hitherto as a yellowish white powder, not crystallized, very acrid, and poisonous. It forms neutral salts hitherto little examined. It may be used in the same affections and in the same manner as veratrine.

l. Staphisine. — This is a substance found along with delphine, and said to be $C_{32}H_{23}NO_4$. It is acrid and poisonous, but is probably only a compound of delphine.

m. Emetine, $C_{57}H_{57}NO_{10}$? — This is the active principle of *ipeacuanha*, the root of *cephaelis ipecacuanha*. When pure, it is a white powder, alkaline, soluble in alcohol and in hot water, insoluble in ether. $\frac{1}{8}$ of a grain acts as an emetic. In a dose of from 2 to 4 grains it is poisonous. Its salts do not crystallize.

n. Chiococcine, and *o. Violine*, are two very similar alcaloids, found in *chiococca ramosa* and *viola odorata*. They are supposed by some to be emetine disguised by a little foreign matter.

p. Strychnine, $C_{34}H_{23}N_2O_7$, or $C_{34}H_{24}N_2O_7$. — This alcaloid is found in *nux vomica*, the seeds of *strychnos nux vomica*, in *St. Ignatius' bean*, the seed of *S. Ignatii*, in the wood of *S. colubrina*, and in the poison called *upas tieuti* derived from *S. tieuti*. It is extracted by decoction with dilute sulphuric acid, precipitating the decoction with milk of lime, and acting on the precipitate, after washing it with cold alcohol, by boiling alcohol, which on cooling deposits the strychnine in very regular, transparent, brilliant crystals. If brucine is present, it remains chiefly in the mother liquid, but the two bases may be separated by converting them into nitrates, and crystallizing; the nitrate of strychnine crystallizes readily, while the nitrate of brucine remains dissolved.

Strychnine is very insoluble, requiring 7000 parts of water. It is so bitter that 1 part gives a very strong and persistent bitter taste to 40,000 parts of water. It dissolves in hot alcohol, although sparingly if the alcohol be pure, and is insoluble in ether. When pure it is only colored yellow by nitric acid; a trace of brucine causes it to be reddened by that acid. It forms crystallizable salts, which are intensely bitter. Their solutions are precipitated white by alkalies, by tincture of galls, and by iodide of potassium, in white crystals by sulphocyanide of potassium, and as yellow powders by solutions of gold and platinum.

Strychnine and its salts, especially the latter, from their solubility, are most energetic poisons. They produce spasmodic motions, and are used in very small doses as remedies in paralysis; they seem to have a specific action on the lower part of the spinal column. The average dose is $\frac{1}{12}$ of a grain. In the event of an overdose, the

best antidote is infusion of galls or strong tea, which also contains tannine.

g. *Brucine*, $C_{14}H_{12}N_2O_7$. — This alcaloid occurs along with strychnine in *nux vomica*, and also in the false angustura bark, the bark of *brucia antidysenterica*. It is prepared as strychnine. Besides the methods above mentioned for separating the two bases, there is another, which is, to boil the mixture with water as long as it dissolves brucine, or till the strychnine is no longer reddened by nitric acid. Brucine forms large transparent crystals, which I have found to become opaque in closely-stopped vials. It is very bitter and poisonous, but much less so than strychnine. It may be used for the same purposes in a rather larger dose. It is reddened strongly by nitric acid, and the red solution becomes violet on the addition of solution of tin. It is thus distinguished from strychnine and morphine. Its salts, for the most part, crystallize with facility.

r. *Jervine*, $C_{60}H_{46}N_2O_3$. — This alcaloid is found in white hellebore, *veratrum album*, along with veratrine, from which it is separated easily, as it crystallizes first from the alcoholic solution; and its sulphate is far less soluble than that of veratrine. It forms a crystalline powder, fusible, insoluble in water, soluble in alcohol, and forming with sulphuric, nitric, and hydrochloric acids, very sparingly soluble salts, so that the solution of the acetate is precipitated by these three acids.

s. *Curarine*. — This alcaloid is obtained from the South American poison called *curari*, which is derived from some plant of the family *strychnaea*. It is a deadly poison when introduced into a wound, but may be swallowed with impunity. The curarine forms a yellowish, amorphous bitter mass, which is more poisonous than the curari which yields it. Its salts are bitter, but do not crystallize.

t. *Corydaline*, $C_{31}H_{22}NO_{10}$? — Found in the root of *corydalis bulbosa* and *C. fabacea*. It forms a light gray powder, very soluble in alcohol, which deposits it in crystals. It is reddened by nitric acid, and forms crystallizable salts with acetic and sulphuric acids.

u. *Carapine*. — Found in *carapus guianensis*. It is a white pearly fusible powder, very bitter, soluble in water and alcohol, insoluble in ether, forming crystallizable salts with hydrochloric and acetic acids.

v. *Cusparine*. — Found in the true angustura bark, that of *bonplandia trifoliata* or *cusparia febrifuga*. It forms fusible octahedral crystals, sparingly soluble in water, very soluble in alcohol.

w. *Daphnine* occurs in the bark of *daphne gnidium* and *D. mezereon*. It is obtained by distilling the infusion with magnesia. It is alkaline and acrid, and forms crystallizable salts with nitric and sulphuric acids, according to Vauquelin. Baer and Gmelin could not obtain it.

x. Bebeerine is the active principle of the bark of the bebeeru tree of Guiana, which seems to be analogous to quinine. It has not been obtained crystallized or colorless, but as a brown mass, the composition of which is not yet ascertained. Bebeerine and its salts are bitter and highly febrifuge. Dr. Douglas MacLagan and Mr. Tilley have found its composition to be the same as that of morphine, namely $C_{25}H_{25}NO_6$?

y. Sanguinarine is found in *sanguinaria canadensis*. It forms a gray powder, which is alkaline and yields red salts. It excites sneezing, and is possibly identical with chelerythrine.

z. Azadirine, found in *melia azedarachta*, is alkaline, forms a crystallizable salt with sulphuric acid, and is powerfully febrifuge.

aa. Capsicine is the active principle of the capsules of *capsicum annuum* or cayenne pepper. It has a resinous aspect and a burning taste, but when quite pure may be crystallized. It forms crystallizable salts with acetic, nitric, and sulphuric acids. It is soluble in alcohol, insoluble (when pure) in ether and in water.

bb. Crotonine occurs in the seeds of *croton tiglium*, and may be obtained from croton oil by boiling it with water and magnesia. It forms crystals, which are fusible, soluble in alcohol, insoluble in water. It forms crystallizable salts with sulphuric and phosphoric acids.

cc. Buxine occurs in boxwood bark. It forms a bitter, brown, amorphous mass, soluble in alcohol, alkaline, and forming a crystalline sulphate. It excites sneezing.

dd. Apyrine, found in *cocos lapidea*. It is a white alkaline powder, forming crystalline salts with acids.

ee. Cynapine, from *æthusa cynapium*. It is crystallizable, soluble in water and alcohol, and forms a crystalline sulphate.

ff. Cissampeline, or *Pelosine*, from *cissampelos pareira*, is a white powder, soluble in alcohol and ether; alkaline, forming soluble salts, of which the hydrochlorate crystallizes.

gg. Oxyacanthine and *Berberine* are two bitter substances found in the barberry, *berberis vulgaris*. The former is decidedly alkaline, and forms crystallizable salts. The latter is bitter, yellow, and feebly, if at all, alkaline. It crystallizes, and is used in dyeing. Its formula is $C_{25}H_{15}NO_{12}$.

hh. Surinamine and *Jamaicine* are two alcaloids, found in *geoffroea surinamensis* and *G. inermis*. Both are crystallizable, and form crystallizable salts; those of the latter are precipitated by tannine and corrosive sublimate.

ii. Piperine, $C_{24}H_{19}NO_5$. — This compound is found in pepper, *piper nigrum*, and *P. longum*. It is crystallizable, soluble in alcohol, very pungent. It is a feeble base, but does form salts, especially double chlorides, containing hydrochlorate of piperine.

kk. Menispermene and *Paramenispermene* are found in *cocculus indicus*, the seed of *menispermum cocculus*. Menispermene is white,

fusible, crystallizable, and forms salts, of which the sulphate crystallizes. Its formula is $C_{16}H_{12}NO_2$.

Paramenispermene has the same composition. It is less fusible, but sublimes at a high temperature. It does not appear to form definite salts. Both are insoluble in water, and soluble in alcohol; and paramenispermene is insoluble in ether.

II. *Harmaline*, $C_{24}H_{15}NO$. — This alcaloid occurs united with phosphoric acid in the seeds of *peganum harmala*. It forms brownish-yellow prisms, bitter, astringent, and acrid, very soluble in alcohol, little soluble in water or ether. It is fusible, and partly volatile. It forms, with acids, yellow crystallizable salts. By oxidizing agents, harmaline is transformed into a red matter, which forms red salts with acids. The harmala red of commerce is the powder of the seeds already transformed into the phosphate of the red harmaline. It is used in dyeing, especially in giving to silk every shade of red, rose color, and pink. It is produced abundantly in the steppes of southern Russia, and is little known out of that country. Fritzsche states that by oxidation harmaline yields two new bases, leucoharmine and chrysoharmine, the composition of which is not given.

mm. *Theobromine*, $C_7H_5N_2O_2$. — This is a crystalline compound, found in cacao, the seed of *theobroma cacao*. It can hardly be called an alcaloid. It is very analogous to the next substance, caffeine.

nn. *Caffeine*, $C_8H_8N_2O_2$. SYN. *Théine*; *Guaranine*. — This remarkable compound is found in coffee, in tea, in *guarana officinalis*, or *paullinia sorbilis*, and in *ilex paraguayensis*. It is best obtained by adding to a decoction of tea a slight excess of acetate of lead, and evaporating to dryness the filtered liquid. The dry mass, mixed with sand, is heated in the apparatus described for benzoic acid, when caffeine is obtained in crystals. Tea yields more than 1 per cent.

Caffeine forms fine white prisms, of a silky lustre, which are soluble in water, alcohol, and ether, bitter, fusible and volatile. It is a feeble base, but forms with hydrochloric acid and sulphuric acid, salts which yield very large crystals.

It is very remarkable, that caffeine should approach so nearly in composition to alloxan and alloxantine. Anhydrous alloxan, plus 1 eq. water, is $C_4N_2H_5O_{11}$, and alloxantine is $C_4N_2H_5O_{10}$, while caffeine is $C_8N_2H_8O_2$, differing from the one by 9, from the other by 8 eq. oxygen.

We shall hereafter see how close a connection can be traced between the bile and the urine; but in the meantime it is a most striking fact, that tea, coffee, Paraguay tea, and guarana, are all used by different and distant nations for the same purpose, namely, as a refreshing and gently stimulating drink, which notoriously promotes the vital functions, while all these plants contain the very

same compound, and that one allied to the bile and the urine, the chief products of the vital metamorphosis. The quantity of caffeine in tea is indeed small, but not too small to have a perceptible influence on the system. Peligot has shown that gunpowder tea contains 6 per cent. of théine (caffeine).

By the action of nitric acid, caffeine yields a crystalline nitrogenized compound, nitrothéine.

Besides caffeine, or théine, tea contains 14 or 15 per cent. of caseine, and the leaves are therefore nutritious, when eaten, as they are by some oriental nations.

e. Alcaloids found in the Animal Organism.

Only two such bases are yet known, namely: urea, already described as occurring in the urine; and kreatinine, which Liebig has detected both in the juice of flesh and in urine, and which will be described as an artificial base, it having been first observed as a product of the action of acids on kreatine.

The following substances have been noticed as alcaloids, but are very little known: castine in *vitis agnus castus*; cicutine in *cicuta virosa*; chærophylline in *chærophyllum bulbosum*; esenbeckine in *esenbeckia febrifuga*; digitaline in *digitalis purpurea*; eupatorine in *eupatorium cannabinum*; euphorbine in *euphorbium*; convolvuline in *convolvulus scammonium*; and pereirine in *pereira bark*.

2. ARTIFICIAL ORGANIC BASES.

Within the last few years, a very considerable number of artificial organic bases have been formed, and the number is rapidly increasing. We have already briefly alluded (page 499) to the sources and mode of preparation of this class of artificial compounds, but we shall here offer a few general remarks on the subject.

All the organic bases, at least all those which are analogous to ammonia in their relation to acids, and the salts of which undergo the ordinary decompositions, contain nitrogen as an essential element. The only organic compounds ever called bases which do not contain nitrogen, are the oxides of ethyle, methyle, and other analogous radicals. But, as formerly observed, these oxides have not the above mentioned characters of ammonia, and their salts do not undergo the usual decompositions. It is true that oxide of cacodyle, which is a perfect base, contains no nitrogen; but cacodyle has all the chemical relations of a metal, and its oxide cannot be classed with the true organic bases.

Nitrogen being an essential constituent of organic bases, it is very natural that ammonia should generally be directly or indirectly concerned in their formation, when they are derived from non-azotized substances. Such is, in point of fact, very often the

case. Thus, for example, bases are formed when ammonia acts on oil of bitter almonds, on furfurole, and on oil of mustard. Again, bases are very often formed by processes of reduction, that is, of deoxidation. For example, aniline, picoline, and leucoline, occur in the destructive distillation, a process of reduction; and thialdine is formed by the action of sulphuretted hydrogen, a powerful reducing agent, on aldehydammonia. Here ammonia is also present; and perhaps the most powerful and successful means at our command for the production of artificial bases, is the combined action of ammonia and sulphuretted hydrogen, or, in other words, the use of sulphide of ammonium.

Bases are obtained when sulphide of ammonia is made to act on nitronaphtalase, nitronaphtalese, nitrobenzole, dinitrobenzole, and nitrotoluole.

In some cases, bases are formed when azotized compounds are heated with potash or with baryta. Thus, isatine, chlorisatine, &c., when heated with potash, yield aniline and chloraniline; leucoline is formed by the action of potash on quinine, &c., melamine and ammeline, when melam is boiled with potash; glycocoll is obtained by heating gelatine with potash, and sarcosine, by heating kreatine with baryta.

As, in most of these cases, hydrogen gas is given off, the process is apparently one of partial oxidation, and we see therefore that reduction is not essential.

Occasionally, acids, when boiled with azotized compounds, give rise to bases. Thus, glycocoll is formed when hippuric acid is boiled with hydrochloric acid; and kreatine, when boiled with strong acids, yields the base, kreatinine.

Artificial urea, already described, is produced by a spontaneous transformation of cyanate of ammonia.

Such are the modes in which artificial bases are formed, as far as we know them at present. Most of them are of very recent discovery, and it is probable that, when more extensively applied, they will yield many new bases. New methods will also be discovered, and we may hope, ere long, to solve the problem of the artificial production of the vegetable alkaloids, a class of compounds of the highest value in medicine.

Already, we have formed artificially two natural bases, namely, kreatinine and urea; and although we have not yet produced quinine or morphine, yet several of the artificial bases approach very closely in composition to that class of bodies. Thus furfurine, $C_{10}H_{12}N_2O_4$, approaches to morphine, $C_{17}H_{19}N_3O_5$. Again, we cannot yet form nicotine, $C_{10}H_{11}N$, or conicine, $C_{15}H_{15}N$; but we have produced aniline, C_6H_7N ; leucoline, $C_{11}H_{13}N$; toluidine, $C_{14}H_{15}N$; seminaphtalidine, $C_{16}H_{17}N$; and naphtalidine, $C_{18}H_{19}N$; and several of these approach to nicotine and conicine as closely in properties as they do in composition.

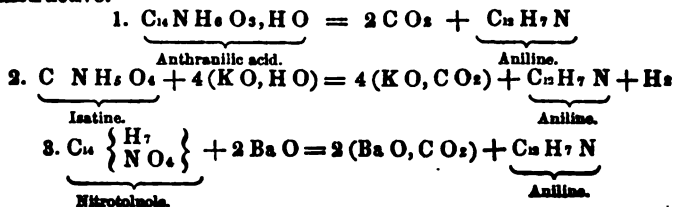
It is important to observe, that we seem to have acquired, in some degree, the remarkable power possessed by the living vegetable, of causing less complex molecules to coalesce so as to give rise to those which are more complex. Thus, when oil of bitter almonds, $C_{14}H_5O_2$, is converted into amarine, $C_{24}H_{15}N_2$, or picrine, $C_{12}N_4H_{12}O_{12}$, 3 eq. must have coalesced into 1; and to yield lophine, $C_{24}H_{15}N_2$, 4 eq. must have been used. Again, when furfurole, $C_5H_5O_2$, yields furfurine, $C_{20}N_2H_{12}O_8$, 2 eq. must have coalesced. Till the discovery of such artificial products, all those organic compounds formed by art were the results of an opposite process, namely, of the breaking down, or resolution, of more complex into less complex molecules. We could imitate nature in her destructive processes, but not in those of a constructive character. Now, to a certain extent, we can do both. It is hardly necessary to point out the importance of the power alluded to, which may hereafter lead to the discovery of the means of artificially producing the highly complex molecules which characterize the animal kingdom. It is in this point of view, that the formation of artificial bases is so interesting, and on this account we have dwelt at some length on the general nature of the processes employed to produce them.

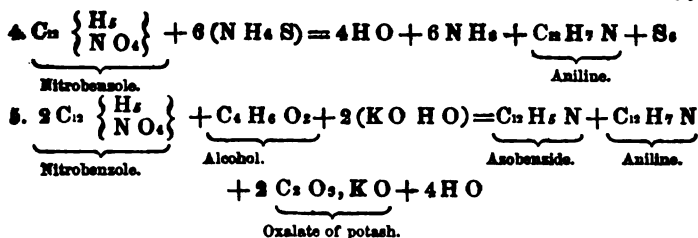
We shall now briefly describe the artificial bases, in so far as they have not hitherto been mentioned, and we shall group them according to their properties and the sources whence they are derived.

a. Volatile Oily Artificial Alkaloids.

Aniline, C_6H_7N . *Syn.* *Crystalline*; *Benzidam*; *Cyanole*. — This base has already been described as derived from indigo, anthranilic acid, and isatine, and as produced also by the action of bases, aided by heat, on nitrotoluole, (protonitrobenzoëne). It is further produced, along with other bodies, when nitrobenzole (nitrobenzide) is distilled with alcohol and potash, and when the same compound is acted on by sulphide of ammonium. Lastly, it occurs in coal-tar, and in the oil obtained by the destructive distillation of animal matter.

We shall here give, in one view, the equations which explain the production of aniline, as no other compound admits of being produced in so great a variety of ways, and all these equations are instructive.





These equations will give the reader some idea of the great variety of processes by which one organic base may be formed, and it is probable that every one of these processes may, if applied to other compounds, give rise to other bases. In fact, this is already the case, as will be seen farther on, with the processes Nos. 2, 3, and 4.

Besides the above sources of aniline there is another, namely, the destructive distillation of azotized matter. That of indigo is explained by No. 1, as anthranilic acid is probably first formed and then destroyed. But aniline is perhaps best obtained from the basic oil of coal-tar. The crude oil of coal-tar is well agitated with hydrochloric acid, which takes up the basic oils in an impure state. They are separated from the acid by ammonia, and consist chiefly of aniline and leucoline. The former is found in that part of the oil which, when it is rectified, passes at near 360° , and it is purified by rectification till it distills at that temperature, combining it with oxalic acid, purifying the oxalate by crystallization, and distilling the pure salt with potash.

Aniline is a colorless oil, highly refracting, of Sp. G. 1.020. It has a burning taste, and a pleasant vinous smell when pure. It turns the delicate purple of the dahlia to green, but does not act on turmeric. A drop of it on fir-wood, moistened with hydrochloric acid, strikes a deep yellow color. It produces a deep but fugitive purple with a solution of bleaching powder. It neutralizes acids, forming salts which have a very great tendency to crystallize: hence the name crystalline. In combining with oxygen acids, aniline, like ammonia, takes up 1 eq. of water, but it combines directly, like ammonia, with hydrogen acids. Like ammonia also, its chloride forms double salts with bichloride of platinum and other analogous salts.

Nitric acid converts aniline into nitrophenisic (picric or nitropicric) acid; and by the action of chlorine, and of chlorate of potash with hydrochloric acid, it is converted into chlorophenisic and chlorophenusic acids, chloranile and trichloraniline. Bromine produces tribromaniline. These transformations prove that aniline belongs to the series of phenyle, as formerly explained. In fact, it has the composition of phenylamide, for $C_{12} H_7 N = C_{12} \left\{ \begin{array}{c} H_8 \\ \text{Ad.} \end{array} \right\}$
See table, p. 495.

The analogy of aniline with ammonia extends beyond what has been above stated; for as ammonia forms, under certain circumstances, such compounds as oxamide and carbamide, the latter only known in combination, so does aniline, under similar circumstances, yield analogous compounds, oxanilide and carbanilide. It even yields formanilide, the analogous compound to which, formamide, is not known. A compound has also been obtained in which the oxygen of carbanilide is replaced by sulphur. — (*Gerhardt. Hoffman*).

Hoffman has also discovered that cyanate of aniline spontaneously passes into aniline-urea, as cyanate of ammonia does into urea.

It has already been mentioned, that by heating chlorisatine, bromisatine, &c., with potash, bases and neutral compounds are obtained in which the hydrogen of aniline is replaced by chlorine and bromine, and that by the action of sulphuretted hydrogen and ammonia on dinitrobenzole, another base, nitraniline, is formed, in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid. A table of these last compounds having been already given (see p. 496), we shall here give only a tabular view of the analogy between aniline and ammonia.

Ammonia in its chloride, &c.	$\left\{ \begin{array}{l} \text{N H}_3 \\ \text{N H}_2, \text{H O} = \\ \text{N H}_4, \text{O} \end{array} \right.$	Aniline in its chloride, &c.	$\left\{ \begin{array}{l} \text{C}_{12} \text{N H}_7 \\ \text{C}_{12} \text{N H}_7, \text{H O} = \\ \text{C}_{12} \text{N H}_8, \text{O} \end{array} \right.$
Ammonia in its sulphate, &c.	$\left\{ \begin{array}{l} \text{N H}_4, \text{O} \\ \text{N H}_4, \text{Cl} + \\ \text{Pt Cl}_2 \end{array} \right.$	Aniline in its sulphate, &c.	$\left\{ \begin{array}{l} \text{C}_{12} \text{N H}_8, \text{O} \\ \text{C}_{12} \text{N H}_8, \text{Cl} + \\ \text{Pt Cl}_2 \end{array} \right.$
Ammonia plati- num salt, &c.	$\left\{ \begin{array}{l} \text{N H}_2, \text{C}_2 \text{O}_2 = \\ (\text{N H}_4, \text{O}, \text{C}_2 \text{O}_2) - 2 \text{H O} \end{array} \right.$	Aniline plati- num salt, &c.	$\left\{ \begin{array}{l} \text{C}_{12} \text{N H}_8, \text{C}_2 \text{O}_2 = \\ (\text{C}_{12} \text{N H}_8, \text{O}, \text{C}_2 \text{O}_2) - 2 \text{H O} \end{array} \right.$
Oxamide		Oxanilide	
Urea	$\left\{ \begin{array}{l} \text{C}_2 \text{N}_2 \text{H}_4 \text{O}_2 = \\ (\text{N H}_4, \text{O}, \text{C}_2 \text{N O}) \end{array} \right.$	Aniline-urea	$\left\{ \begin{array}{l} \text{C}_{14} \text{N}_2 \text{H}_8 \text{O}_2 = \\ (\text{C}_{12} \text{N H}_8, \text{O}, \text{C}_2 \text{N O}) \end{array} \right.$

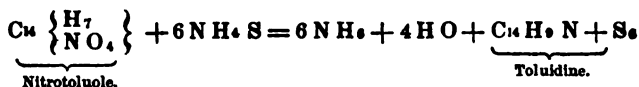
It is impossible, after considering the facts exhibited in the above table, to doubt the perfect analogy, existing in all their chemical relations, between ammonia and aniline. Our space will not admit of farther details concerning the remarkable derivatives of aniline here mentioned.

Picoline, $\text{C}_{12} \text{H}_7 \text{N}$, is another volatile oily base, isomeric with aniline, lately discovered in coal-tar by Dr. T. Anderson. It is found in the more volatile portion of the basic oil, boiling at 272° . It has no action on bleaching-liquid or on fir-wood. It is a powerful base; and as it has a strong penetrating odor, it is probably identical with the odorine of Unverdorben, which, however, was not obtained in a state of purity. Under naphthaline, we shall return to the isomerism of aniline and picoline.

Leucoline. *Syn. Quinoline*, $\text{C}_{12} \text{H}_9 \text{N}$. — This base is found in the least volatile portion of the basic oil of coal-tar, and is also

formed when quinine, cinchonine, strychnine, and thialdine are heated with potash. It has a disagreeable smell, and boils at 460°. Its Sp. G. is 1.081. It neutralizes acids, forming crystallizable salts. Its refractive and dispersive power is as high as that of bisulphide of carbon.

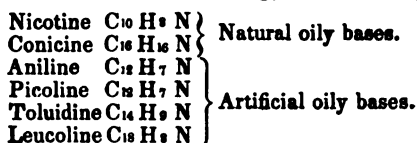
Toluidine, $C_{14}H_9N$. — This base is formed by the action of sulphuretted hydrogen and ammonia or nitrotoluole, as aniline is from nitrobenzole. It is derived from the fundamental compound of the series, toluole, $C_{14}H_8$, as aniline is from benzole or phène, $C_{12}H_6$.



Toluidine is, in taste and smell, very similar to aniline; and, although solid and crystalline at the ordinary temperature, it melts at 104° to a highly refracting oil, which boils at 388°. It also turns fir-wood yellow, with the aid of hydrochloric acid. It belongs, therefore, evidently to the class of volatile oily bases, none of which, as we have seen, contain oxygen.

With bromine, toluidine yields a crystalline body, $C_{14} \left\{ \begin{array}{c} H_6 \\ Br_3 \end{array} \right\} N$; and ohlerine appears to form an analogous compound. These products correspond to tribromaniline and trichloraniline.

Let us now place together the natural and artificial oily bases, and we shall be struck with the analogy in their composition.



The analogy extends to the properties of these bases; for aniline is said to be poisonous, and we have seen that in all, the external characters are similar.

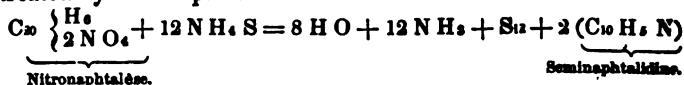
Aniline and toluidine have been formed from the two carbohydrogens, benzole $C_{12}H_6$, and toluole, $C_{14}H_8$, by first converting them into nitrobenzole and nitrotoluole, and then treating these compounds as above explained. It is evident, therefore, that, if we had the carbohydrogens, $C_{10}H_6$ and $C_{16}H_{14}$, we might expect to be able to form nicotine and conicine.

b. Bases derived from Naphtaline.

These bases are formed in a manner quite analogous to that in which aniline is produced from benzole, and toluidine from toluole. The carbohydrogen is first converted, by the action of nitric acid, into a compound in which H is replaced by NO_2 ; and the new product, according to the ingenious process devised by Zinin, is

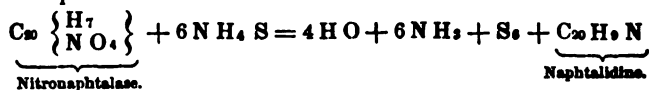
dissolved in alcohol, and acted on by ammonia and sulphuretted hydrogen.

Seminaphtalidine, $C_{10}H_8N$, is obtained when nitronaphtalène is treated by Zinin's process.



It forms reddish-yellow prisms, of metallic lustre, insoluble in water, soluble in alcohol and ether, and yielding crystallizable salts with acids.

Naphtalidine, $C_{10}H_8N$, is produced, in a similar way, from nitronaphtalase.

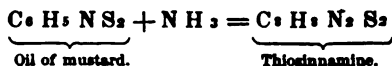


It appears in the form of colorless crystals, soluble in alcohol and ether, and combines with acids, yielding crystallizable salts.

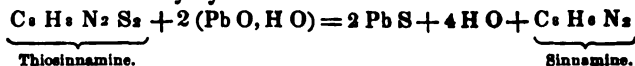
c. Bases derived from Oil of Mustard.

These bases have already been briefly described under the head of oil of mustard. They are as follows :

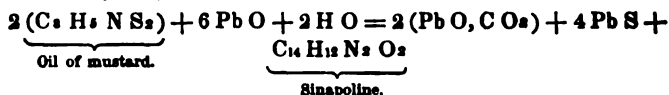
1. *Thiosinamine*, $C_8H_7N_2S_2$, formed by the action of ammonia on oil of mustard.



2. *Sinamine*, $C_8H_7N_2$ or C_4H_3N , formed when thiosinamine is acted on by hydrated oxide of lead.



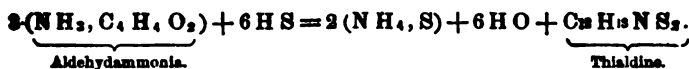
3. *Sinapoline*, $C_{14}H_{13}N_2O_2$, formed when oil of mustard is acted on by baryta or oxide of lead.



The above equations will serve to explain the formation of these remarkable compounds, all of which, it will be seen, are produced by the action of bases, and one of which contains sulphur, an element hitherto only known to occur in one other organic base, namely, thialdine.

d. Bases derived from Aldehyde.

These bases are of recent discovery, and have been briefly mentioned under *Aldehyds*. For the convenience of the reader, we here repeat the equation which illustrates their formation.



Selenaldine, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{Se}_2$, is formed by a perfectly analogous process.

c. Bases derived from Melam.

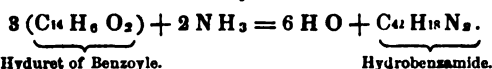
These bases have been already described, p. 322; but we shall here repeat the equation, for the sake of easy reference. When melam is boiled with potash it yields two bases, melamine and ammeline.



f. Bases derived from Oil of Bitter Almonds.

Two of these bases have also been mentioned, p. 350, and another has since been described. We shall now, as was promised under *Amarine* and *Lophine*, give a brief account of these compounds.

Amarine, $\text{C}_{14}\text{H}_6\text{N}_2$, is formed from hydrobenzamide, with which it is isomeric or polymeric, by boiling the latter compound with potash. The formation of hydrobenzamide is thus explained:



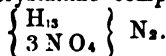
When hydrobenzamide, a neutral compound, is boiled with potash, a new arrangement of particles takes place, and a base is the result. It is possible that hydrobenzamide is really $\frac{\text{C}_{12}\text{H}_{12}\text{N}_2}{3}$; or, if we represent $\frac{\text{N}}{3}$ ($\frac{1}{3}$ of N) by Az, then hydrobenzamide will be $\text{C}_{14}\text{H}_6\text{Az}_2$; that is, hyduret of benzoyle, in which O_2 is replaced by Az_2 . In this case 3 eqs. of hydrobenzamide, $\text{C}_{14}\text{H}_6\text{Az}_2$, coalesce to form 1 eq. of amarine; $3(\text{C}_{14}\text{H}_6\text{Az}_2) = \text{C}_{14}\text{H}_6\text{N}_2$.

Amarine forms fine white needles, soluble in hot alcohol, insoluble in water. It has all the characters of a powerful organic base.

Lophine, $\text{C}_4\text{H}_{16}\text{N}_2$, is formed when hydrobenzamide is distilled. Ammonia is given off, then a fragrant oil and a mass is left, from which ether removes a substance not yet examined, leaving the lophine undissolved. Lophine is soluble in alcohol with the aid of acids, and is precipitated by ammonia. It forms fine silky crystals, which possess all the characters of a base. We cannot as yet represent its formation accurately, because the accompanying products have not yet been properly investigated; but it is evident that if hydrobenzamide be $\text{C}_{14}\text{H}_6\text{N}_2$, then 2 eq. at least must be required to yield one of lophine; and if hydrobenzamide be

$C_{14}H_5Az_2$, as suggested under *Amarine*, less than 4 eq. could not furnish one of lophine.

By the action of hot nitric acid, lophine yields a yellow crystalline compound, trinitolophyle, the formula of which is C_8



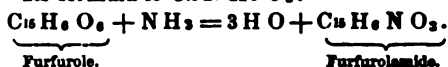
Picrine. SYN. *Picryle*, $C_{15}H_{15}NO_4$. — Is formed when the mass produced by acting on oil of bitter almonds by sulphide of ammonium is distilled. It is one of a large number of products, not fully examined, so that its formation cannot be represented in the usual way. It must be produced, however, by the coalescence of 3 eq. of the oil. It forms colorless octahedrons, insoluble in water. It appears to have the properties of a weak base.

By the action of nitric acid, picrine is converted into a yellow crystalline powder, trinitropicryle, $C_{12} \left\{ \begin{array}{c} H_{12} \\ 3NO_4 \end{array} \right\} NO_4$.

The formation of the three preceding bases is very important, in reference to the views expressed in the general remarks on the artificial bases, as they are good examples of the power of building up complex molecules from such as are less complex.

g. Base derived from Furfurole.

Furfurole, $C_{15}H_5O_6$, is a volatile oil obtained by heating bran with sulphuric acid. When this oil is acted on by ammonia, it yields a crystalline compound, furfurolamide, analogous to hydrobenzamide. Its formula is $C_{15}NH_5O_5$.



Furfurine, $C_{30}H_{15}N_2O_6$, is a base, formed when furfurolamide is dissolved in hot potash, just as amarine is formed from hydrobenzamide. Here 2 eq. of furfurolamide coalesce to form 1 eq. of the base.

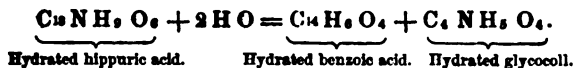
Furfurine is a powerful base, soluble in hot water, and crystallizable. It expels ammonia from its salts when heated with them, and forms crystalline salts with acids. In composition it approaches nearly to several vegetable alkaloids.

h. Bases derived from Narcotine.

These bases, cotarnine, $C_{25}H_{15}NO_6$, and narcogenine, $C_{26}H_{16}NO_{10}$, have been already described under *Narcotine*.

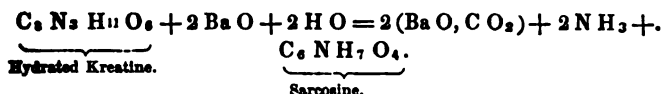
i. Bases derived from Animal Products.

Glycocol. SYN. *Sugar of gelatine*, $C_4NH_5O_4$. — This remarkable compound was first obtained among the products of the decomposition of gelatine by boiling with potash or with acids. But Dessaignes has lately discovered that it is best prepared by heating hippuric acid with hydrochloric acid, when water is taken up, and benzoic acid is the only other product.



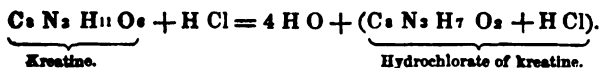
It forms large transparent crystals, soluble in water, and very sweet. It has the properties of a base, and neutralizes acids, forming beautifully crystallized salts; but Horsford has shown that it also combines with bases and neutral bodies. By its composition, it is closely related to many different compounds, and probably plays an important part in the animal organism.

Sarcosine, $C_5H_7O_4$. — This base is formed, along with urea, when kreatine is boiled with baryta; but the urea is resolved into carbonic acid and ammonia.



Sarcosine forms right rhombic prisms, soluble in water, fusible, and volatile at a heat not much beyond 212° . It neutralizes acids, and has all the characters of an alcaloid. It is isomeric with urethane, or carbamate of oxide of ethyle, and with lactamide, or anhydrous lactate of ammonia.

Kreatinine, $C_8N_3H_7O_5$. — This base occurs in the juice of flesh, and in urine — (*Liebig*); but it was first observed as a product of the action of acids on kreatine. When kreatine is boiled with hydrochloric acid, 4 eq. of water are given off, and the new base is found combined with the acid.



Kreatinine is separated from the hydrochlorate by means of oxide of lead. It forms prisms, soluble in water and alcohol. It combines with acids, yielding crystallizable salts, and it has all the characters of a powerful organic base.

Kreatinine is important, as occurring in the animal organism. Under the urine and the juice of flesh we shall return to it. The substance discovered by Pettenkofer in urine, is, according to Liebig, a mixture of kreatinine with kreatine.

We have now gone through the artificial as well as the natural alcaloids, and the present is the proper place to say a few words concerning the constitution of this class of compounds. Of the constitution of the vegetable bases nothing certain is known; but the modes of formation of the artificial alcaloids have suggested certain views as possible or even probable.

In the first place, it may be considered very probable that all alcaloids are formed by substitution from other substances, as for example, aniline from nitrobenzole, and toluidine from nitrotoluole.

In the next place, some of the alcaloids may be viewed as compounds of amide, as, for example, aniline, which has the composition of phenylamide :



The other artificial bases analogous to aniline may be regarded in the same way ; leucoline as $C_{12}H_9 + NH_2$, or toluidine as $C_{14}H_7 + NH_2$; being derived, on this view, by substitution of amide either for hydrogen in the carbohydrogens, C_6H_5 , C_6H_7 , and $C_{14}H_9$, or for nitrous acid in the compounds, $C_6H_5 \left\{ \begin{smallmatrix} H_5 \\ NO_2 \end{smallmatrix} \right\}$, $C_6H_7 \left\{ \begin{smallmatrix} H_7 \\ NO_2 \end{smallmatrix} \right\}$ and $C_{14}H_9 \left\{ \begin{smallmatrix} H_9 \\ NO_2 \end{smallmatrix} \right\}$. This class of alcaloids, which contain no oxygen, seem to have the simplest constitution.

But, thirdly, there is among the artificial alcaloids a substance which may be taken as the type of a somewhat more complex class, in which the hydrogen of the fundamental compound of the series has been replaced by some compound of nitrogen and oxygen. This substance is nitraniline, which is $C_6H_5N_2O_4 = C_6H_5 \left\{ \begin{smallmatrix} H_5 \\ NO_2 \end{smallmatrix} \right\} N$.

Fresenius suggests that many of the natural alcaloids, containing 4 eq. of oxygen and 2 of nitrogen, may have a constitution analogous to that of nitraniline, in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid. For example, strychnine, $C_{28}H_{27}N_2O_4$, may be $C_{28}H_{25} \left\{ \begin{smallmatrix} H_{25} \\ NO_2 \end{smallmatrix} \right\} N$. Quinine, menispermene, ~~star~~ phisaine, and delphine, may all be associated with strychnine.

Chelidonine, $C_{20}H_{17}N_2O_4$, may be according to Fresenius, binitrichelidonine, $C_{20}H_{15} \left\{ \begin{smallmatrix} H_{15} \\ 2NO_2 \end{smallmatrix} \right\} N$; 2 eq. of hydrogen being replaced by 2 eq. of hyponitrous acid.

Where the alcaloid contains 2 eq. oxygen and two of nitrogen, the replacing body may be deutoxide of nitrogen. Thus, caffeine, $C_8H_{10}N_4O_2$, may be nitre-caffeine, $C_8H_8 \left\{ \begin{smallmatrix} H_8 \\ NO_2 \end{smallmatrix} \right\} N$; and to this class would belong cinchonine and sinapoline. Urea may be added, as it may be $C_2H_4 \left\{ \begin{smallmatrix} H_4 \\ NO_2 \end{smallmatrix} \right\} N$.

Another class may contain protoxide of nitrogen as replacing substance. Thus, harmaline, $C_{12}H_{13}N_2O$, may be nitra-harmaline, $C_{12}H_{11} \left\{ \begin{smallmatrix} H_{11} \\ NO \end{smallmatrix} \right\} N$; and theobromine, $C_7H_7N_2O_2$, may be binitra-theobromine, $C_7H_5 \left\{ \begin{smallmatrix} H_5 \\ 2NO \end{smallmatrix} \right\} N$.

Lastly, hydrogen may even be supposed to be replaced by nitric acid ; and, on this supposition, jervine, $C_{20}H_{15}N_2O_3$, might be nitru-jervine, $C_{20}H_{13} \left\{ \begin{smallmatrix} H_{13} \\ NO_2 \end{smallmatrix} \right\} N$.

The bases above mentioned, if such be their true constitution, are derived from radicals containing no oxygen, as aniline from benzole, &c. But there are others, which are probably derived from radicals containing oxygen. Such bases are morphine, codeine, narcotine, and others. Of these, however, in this point of view so little is known, that, as Fresenius observes, it is safest for the present to consider them as simple alcaloids, analogous to aniline, nicotine, or sinnamine.

The views of Fresenius have a high degree of probability, and will probably aid in enabling us to discover the true nature of the alcaloids. He points out that, on his theory, various facts connected with the alcaloids are easily explained. Thus, for example, it is easy to see, on his theory, that when heated with potash ammonia is not given off; and their power of saturation cannot be proportional to their amount of oxygen or of nitrogen, as it is well known not to be. On the other hand, it appears to be proportional to the amount of nitrogen which is not in the form of an oxygen compound, such as N O , N O_2 , N O_3 , N O_4 , or N O_5 . This nitrogen, generally, perhaps always, amounts to 1 eq. in 1 eq. of the base, as may be seen in Fresenius' formulæ. The simple alcaloids, such as aniline, contain only that 1 eq. of nitrogen, just as ammonia does.

It must here be remarked that the alcaloids all appear to be of the same general type with ammonia, and that, like ammonia, they unite directly with hydrogen acids, while, to combine with oxygen acids, they take up 1 eq. of water. This leads to the conclusion, that if, in the case of ammonia, there is formed a compound analogous to metals, ammonium, which unites with salt radicals, while its oxide combines with oxygen acids, the same is probably true of the alcaloids. Thus, when ammonia acts on hydrochloric acid, we have $\text{N H}_3 + \text{H Cl} = \text{N H}_4 + \text{Cl}$, chloride of ammonium, and when aniline combines with the same acid, we may suppose the change to be analogous: $\text{C}_{12}\text{H}_7\text{N} + \text{H Cl} = \text{C}_{12}\text{H}_8\text{N Cl}$, chloride of anilium. Again, sulphate of ammonia, $\text{N H}_3, \text{H O}, \text{S O}_3$, is usually considered to be sulphate of oxide of ammonium, $\text{N H}_4, \text{O} + \text{S O}_3$, and so, in like manner, sulphate of aniline, $\text{C}_{12}\text{H}_7\text{N}, \text{H O}, \text{S O}_3$, is probably sulphate of oxide of anilium, $\text{C}_{12}\text{H}_8\text{N}, \text{O} + \text{S O}_3$. If true of one, this is probably true of all.

Such is the present state of our knowledge with regard to the alcaloids; and, although it is still very imperfect, yet it is evident that we are now making some progress in this department of science, and may hope speedily to advance much farther.

We now come to a class of compounds, very widely distributed in the vegetable kingdom, but not exhibiting the same varieties as the class hitherto described, and not characterized by the same marked properties. This is the class of neutral or indifferent non-

azotized bodies, which are never poisonous, hardly even possessed of medicinal properties, and exhibit no striking chemical characters. It includes starch, gum or mucilage, pectine or vegetable jelly, and woody fibre or lignine, with their derivatives. We can only describe them briefly.

INDIFFERENT NON-AZOTIZED COMPOUNDS.

1. STARCH. $C_6H_{10}O_5$.

This very important compound is universally diffused in the vegetable kingdom. It occurs in seeds, as in those of wheat and other cerealia, and also in the leguminosæ; in roots, as in the tubers of the potato; in the stem or pith of many plants, as in *sagus rumphii*; in some barks, as that of cinnamon; and in pulpy fruits, such as the apple. Finally, it is contained in the expressed juice of most vegetables, such as the carrot, in a state of suspension, being deposited on standing.

It is chiefly extracted from wheat flour (common starch); from potatoes (potato starch); from the root of *jatropha manihot*, (tapioca); from that of *maranta arundinacea* (arrow-root); from the stem and pith of *sagus farinifera rumphii* (sago); the substances known by these different names being all essentially the same.

When flour is kneaded with water in a cloth, the water carries off the starch in suspension, and deposits it on standing, leaving behind the gluten. By a similar process starch is purified from the cellular substance and other matters mixed with it in potatoes, which are rasped, and then treated with water as above. Sago, being finally dried at a somewhat high temperature, acquires a horny and translucent appearance.

Pure starch is a snow-white powder, of a glistening aspect, which makes a crackling noise when pressed with the finger. It is composed of transparent rounded grains, the size of which varies in different plants. Those of the potato are the largest, those of the leguminosæ, as peas, are very small, and those of wheat and rice are the smallest. Starch is insoluble in cold water, alcohol, and ether; but when heated with water it first becomes viscid, and is then converted into a kind of solution, which, however, is not complete, but is rather formed by the swelling of the grains of starch into a mucilaginous mass. On cooling, the whole forms a stiff, semi-opaque jelly. If dried up, this yields a translucent mass, which softens and swells into a jelly with water, like tragacanth. The solution, or mixture of starch and water, has the remarkable property of striking a deep blue color with free iodine. This appears to be owing not so much to a chemical or definite combination, as to the mechanical division of the iodine; there is even reason to think that the blue color is that of iodine finely divided, adhering to the starch as a dye does to the fibres of cloth.

When starch is warmed with water, to which has been added either some infusion of malt or some diluted acid, the viscosity of the mixture disappears, and the fluid solution is no longer colored blue by iodine. As soon as this is the case, the whole of the starch has disappeared, and has been converted into a soluble gum called dextrine, from its power of causing the plane of polarization to deviate to the right. According to the proportion of malt or of acid, and the temperature employed, the change is more or less rapid; and when the action is continued the dextrine is in its turn converted into glucose, or grape sugar, which from this circumstance is also called starch sugar.

In contact with oil of vitriol, starch appears to form a compound or coupled acid, sulphoamidic acid. Strong nitric acid, rubbed up with potato starch, dissolves it, forming a viscid liquid, from which water precipitates a white explosive compound, called xyloidine. This compound has some of the properties of gum tragacanth, but it contains the elements of nitric acid, and has not yet been fully investigated. According to Pelouze, its formula is $C_6H_4O_4 + NO_2$; according to Ballot, it is $C_{12}H_{12}N_2O_8$; but more recent researches tend to show that the formula of xyloidine is C_{12}

$\left\{ \begin{array}{l} H_2 \\ 2NO_2 \end{array} \right\} O_{10}$; that is, starch, in which 2 eq. of hydrogen are replaced by 2 eq. of nitrous acid. When starch is distilled with moderately strong sulphuric acid, it yields carbonic acid, formic acid, and a pungent volatile oil, hitherto very little examined.

The blue compound of iodine and starch is best prepared by adding to the liquid filtered from the viscid paste obtained by boiling starch with water, first iodide of potassium, and then solution of chlorine, as long as it causes a blue precipitate, which is to be washed till the water passes deep blue, and dried in vacuo. Its color is so intense as to be nearly black. It does not appear to be a compound in definite proportions. The best method of using starch as a test for iodine in mineral waters, &c., is to add to the water some starch paste, and then a little nitric acid or chlorine. The latter is best added in the form of gas, its weight allowing it to be poured like water; while in this way we are less likely to add an excess which would destroy the blue color. Or we may place in the bottom of a vial the liquid to be tested, adding a little oil of vitriol, and suspending from the stopper a slip of paper moistened with starch paste. After a time, if iodine be present the paper will exhibit a tinge of blue. By these tests ~~with~~ ^{the} part of iodine in a liquid may be detected.

With bromine, starch forms an orange-yellow precipitate, which cannot be dried without decomposition.

Dextrine is best obtained by heating to about 120° a mixture of 20 parts of starch paste and 1 part of strong infusion of malt, until iodine no longer colors the mixture blue. The addition of

strong alcohol now precipitates the dextrine as a thick syrup, while any sugar remains dissolved. When dried, dextrine much resembles gum, from which, however, it differs in the extreme facility with which it is converted into sugar when warmed with dilute sulphuric acid or infusion of malt, and by not yielding mucic acid when acted on by nitric acid. The composition of dextrine is the same as that of starch. In fact, dextrine is supposed by some to be the substance which is contained in the grains of starch, inclosed in an insoluble membrane, which is burst in the process of conversion of starch into dextrine, or solution of starch, by means of acids and infusion of malt. The substance present in the malt which has the property of effecting this change, is called diastase. It contains nitrogen.

According to other observers, the grains of starch are composed of concentric layers of one and the same substance (dextrine?), the outer layer being insoluble in water. As starch is found to contain a small proportion of matter analogous to wax or caoutchouc, we may suppose that the presence of this matter in the outer layer is the cause of its insolubility, or that the whole mass of the grains is, by its means, rendered insoluble, and endowed with the property of swelling up with water to a paste or jelly. Dextrine will then be purified, and consequently soluble, matter of starch. If the outer coat be different from the contents of the grains, it has still the same composition; for analysis shows no difference between starch, dextrine, and the insoluble matter left on the filter when starch is boiled with diluted acids.

Leiocome. — This name is given to a substance having the properties of gum, which is prepared by simply roasting or torrefying starch at about 300°. It is, in fact, capable of being used, instead of gum in calico-printing, and is made on the large scale. It has a yellowish-brown color. It is probably dextrine, more or less pure, generally containing some undecomposed starch. When well made it dissolves in cold water like gum.

Inuline, $C_{36}H_{62}O_{31}$? $C_{36}H_{64}O_{31}$? $C_{36}H_{62}O_{31}$? — This is a substance analogous to starch, in the roots and tubers of *inula helenium*, *dahlia variabilis*, *helianthus tuberosus*, and many other synanthorous plants, which do not yield ordinary starch.

It is extracted from the roots by boiling water, and is deposited by the concentrated decoction as a brittle white mass, formed of crystalline grains, or as a fine powder. It is tasteless, insoluble in cold, very soluble in hot water. Diluted sulphuric acid, with the aid of heat, rapidly converts it into grape sugar, from which, like starch, it differs only by a certain amount of the elements of water. This may be seen by the above formulæ, which represents inuline from different plants, as it exists in its compounds with oxide of lead. It would appear to differ in different vegetables, but always retaining the character of this class of bodies, namely,

the presence of hydrogen and oxygen in the proportions to form water. Iodine colors it slightly brown.

Lichenine, $C_{18}H_{10}O_{10}$. — This is a variety of starch found in *Lichen islandicus*, or Iceland moss. It forms, when pure, a nearly colorless, tasteless mass, which swells up into a transparent jelly with cold water, and dissolves entirely in hot water. When its solution is boiled it forms pellicles like milk, which adhere to the vessel. Its solution is not colored by iodine, but the jelly is rendered blue by that test. By diluted and boiling sulphuric acid it is converted into sugar; by nitric acid, into oxalic and saccharic acids. It has the composition of starch.

Saponine is the name given to a variety of starch obtained from the root of *saponaria officinalis*. Its properties are little known.

2. GUM.

This name was formerly given to almost all exudations from plants. It is now limited to certain rather abundant substances, which are solid, uncrystallizable, transparent, or translucent, colorless, or nearly so, tasteless, inodorous, soluble in water, or at least softening in it, and insoluble in alcohol, ether, fat, and volatile oils. They yield mucic acid when acted on by nitric acid. They may be divided into gums which dissolve in cold water, (arabine, mucilage), and gums which only swell up to a jelly, (tragacanth or bassorine, cerasine, pectine). Arabine and cerasine contain oxygen and hydrogen in the proportion to form water: the other gums are nearly analogous in composition.

Arabine, or gum arabic, is found as an exudation from several species of acacia. What is called gum senegal is essentially the same. It is nearly colorless, transparent, hard, and brittle, and has a mild taste. It is very soluble in cold water, and forms a viscid mucilage, from which alcohol precipitates the gum. The diluted solution is precipitated by silicate of potash, subacetate of lead and protonitrate of mercury. When a mixture of gum, water and sulphuric acid is kept for some time at a temperature near boiling, it is converted into grape sugar. The composition of gum is $C_{12}H_{22}O_{11}$, that is, the same as that of cane sugar, which accounts for the transformation. Arabine yields 2 or 3 per cent. of ashes, containing a good deal of lime.

Mucilage is the name given to a substance resembling gum, found in many vegetables, such as linseed, *althæa*, and others. It differs from arabine in being less hard when dry, and less transparent. It would appear, however, that the mucilage of *althæa*-root is essentially starch inclosed in cells formed of woody fibre or cellulose. The different mucilages are resolved into grape sugar by being heated with dilute sulphuric acid, and therefore may be considered as containing, like starch and arabine, water plus carbon. Since all these mucilages contain much mineral matter,

the mucilage of linseed, for example, leaving 11 per cent. of ashes rich in lime, it is probable that their peculiar qualities depend on the presence of phosphate of lime or other salts of lime, disguising either starch or arabine.

Bassorine is the name given to a substance which forms the chief part of gum tragacanth and of gum bassora, and also, according to some, of salep, a mucilaginous substance, obtained from the bulbs of *orchis mascula*. According to Schmidt, however, salep is really formed of swelled up grains of starch.

Pure bassorine resembles arabine in appearance, but is less transparent, and instead of dissolving in cold water, only swells up to a very great extent, forming a viscid mass. Its composition is analogous to that of arabine, and by digestion with diluted sulphuric acid, it is transformed, like salep, into grape sugar and cellulose. Cerasine is the name given to that part of the gum of the cherry, plum, or almond trees, which is insoluble in cold water. It is probably identical with bassorine, or with salep.

During what is called the viscous fermentation, which takes place in certain sweet vegetable juices, as that of beet-root, there is formed, along with lactic acid and mannite, a mucilaginous compound, which causes the viscosity. When dried, it has nearly the characters and composition of arabine.

Pectine is the substance which causes the juice of some pulpy fruits, as apples and pears, to coagulate or gelatinize when mixed with alcohol, by which the pectine is precipitated. When dried, it resembles gum or isinglass, and forms a jelly with water. By the action of nitric acid it yields oxalic and mucic acids. It generally yields about 8 per cent. of ashes, containing much phosphate of lime. In contact with alkalies, it is transformed into pectic acid. Pectic acid is easily obtained from many vegetables, as, for example, rasped carrots, by washing them well with distilled water, and then boiling 50 parts of the squeezed residue with 300 of water and 1 of potash. The pectate of potash is deposited as a jelly in the filtered liquid on cooling. Either this salt or the pectate of lime may be decomposed by diluted hydrochloric acid, which leaves the pectic acid as a jelly, which dries up into transparent laminæ, insoluble in water, but very soluble in alkalies. From these solutions acids precipitate it as a jelly. In this form it is slightly soluble in boiling water, but the solution gelatinizes on the addition of acids, salts, alcohol, or sugar. It is supposed not to exist ready formed in the plants, but to be produced by the action of alkalies on pectine.

The alkaline pectates, when dry, form gummy solids, soluble in water. Alcohol causes the solution to gelatinize, and even an excess of potash or soda has the same effect. The earthy and metallic pectates are gelatinous and insoluble. When dried, pectine, pectic acid, and all the pectates, assume a cellular structure, so to speak.

The jelly formed in currant juice, as well as other juices, by the addition of sugar, is pectine or pectic acid. The boiling of such juices probably promotes the formation of jelly; for it has been shown that when the insoluble part of unripe currants, after being washed, is boiled with water acidulated with a vegetable acid, a considerable quantity of pectine is formed, probably by a transformation of the cellular tissue.

The composition of pectic acid is not fully ascertained. According to Regnault it is $C_{18}H_2O_{11}$, or $C_{18}H_7O_{10}, H_2O$. According to Mulder, it is $C_{12}H_2O_{10}$. But the researches of Chodnew have led him to adopt the formula $C_{28}H_{18}O_{24}, 2H_2O = C_{28}H_{20}O_{22}$. In all the formulæ there is an excess of oxygen over hydrogen.

The whole subject of the mucilaginous compounds, including pectine and pectic acid, is still very obscure and requires renewed investigation.

Apiine is a substance analogous to pectine, found in parsley, *apium graveolens*.

Glycyrrhizine is the name given to a substance resembling both sugar and gum, which is the chief ingredient in liquorice, the juice of the root of *glycyrrhiza glabra*. It is soluble in hot water, and gelatinizes on cooling. Its taste is sweet and also acid; but it does not, like sugar, undergo the vinous fermentation. Its formula is said to be $C_{18}H_{18}O_8$.

Sarcocolline is a gummy matter found in the sarcocolla of commerce, which is the dried juice of *penca mucronata*. It is soluble in alcohol and water, and has a taste both sweet and bitter. Formula, $C_{28}H_{18}O_{10}$? or $C_{28}H_{22}O_{14}$?

3. WOODY FIBRE.

The skeleton of plants, after everything soluble in water, alcohol, ether, diluted acids, and diluted alkalies has been removed, is called woody fibre. It varies in aspect and in composition as obtained from different plants. That of box or willow, when dried, is $C_{12}H_2O_8$; that of oak is $C_{28}H_{18}O_{22}$; and that of beech is intermediate between these two. All varieties, however, may be represented as composed of carbon plus water.

Recent researches have shown that wood is composed of two parts: 1. cellulose, which forms the parietes of the vegetable cells; and 2. lignine, which fills those cells, or forms an incrustation on their walls. The latter dissolves in strong nitric acid; the former is left undissolved. Again, oil of vitriol dissolves cellulose without blackening, and it appears to convert it into dextrine, with which it agrees in composition; while lignine separated from cellulose is said to contain $C_{28}H_{18}O_{22}$.

Linen, cotton, and paper are woody fibre, more or less. All these substances, and others of similar nature, like tow and sawdust, yield, when acted on

explosive compounds, analogous to that obtained from starch, already described under the name of xyloidine.

Gun-cotton is best made by immersing for two minutes 1 part of clean dry cotton wool in about 10 parts of an acid composed of equal volumes of oil of vitriol, Sp. G. 1.840, and nitric acid, Sp. G. 1.510. It is then gently pressed, to expel as much as possible of the acid, rapidly washed with water, till the water runs off tasteless, and dried by a gentle water heat. 100 parts of dry cotton are found, when thus treated, although little changed in appearance, to have increased in weight to 169.5 parts. Of this weight 102.5 parts are nitric acid, and 67, or two-thirds, of the original weight, are derived from the cotton, and represent what may be called anhydrous cotton, the remaining one-third, or 33 parts, having been lost in the shape of water, which has combined with the acid.

According to Porret and Teschemacher, anhydrous cotton is $C_{12}H_8O_8$, and gun-cotton is $C_{12}H_8O_8 + 4NO_2$, which corresponds to the above proportions. But the gun-cotton may also be $C_{12}H_8O_{12} + 4NO_4$, or $C_{12}H_8O_{16} + 4NO_2$; while xyloidine, whether from starch or from woody fibre, is $C_{12}H_8O_8 + 2NO_2$, $C_{12}H_8O_{10} + 2NO_4$, or $C_{12}H_8O_{12} + 2NO_2$. This explains the superior explosive force of gun-cotton, the combustion of which must be much more complete. In fact, when exploded, it leaves no visible residue.

It is not probable that gun-cotton will supersede gunpowder for fire-arms, as it is expensive, and its preparation is somewhat uncertain. But when well made, it explodes so rapidly that it will probably be found advantageous in the blasting of rocks.

By the continued action of acids or of hot alkalies, woody fibre yields a substance which is colored blue by iodine. Linen, cotton, or paper, all of them different forms of woody fibre, when moistened with pretty strong sulphuric acid, are converted apparently first into dextrine, and afterward into grape sugar. When heated with a more diluted acid, linen yields an amylaceous pulp hardly soluble in water, the composition of which is $C_{12}H_{10}O_{10}$.

When exposed to air and moisture, wood undergoes eremacae-sis, being slowly converted into a friable mass, which contains a larger proportion of carbon than the original wood. It would appear that the oxygen of the atmosphere combines with the hydrogen, and that carbon and oxygen are given off from the residue as carbonic acid, CO_2 . As the residue is found still to consist of carbon and water, it is evident that for every equivalent of carbon removed, there are separated 2 eq. of oxygen and hydrogen, so that the proportion of carbon to water in the residue is constantly increasing. Woody fibre $C_{24}H_{32}O_{24}$ will thus yield first a residue of $C_{24}H_{20}O_{10}$; then $C_{24}H_{18}O_{12}$, $C_{24}H_{16}O_{14}$, and so on. When air is left in contact with moist wood, its oxygen is removed and replaced

by an equal volume of carbonic acid. This is one chief source of the insalubrity of marshy districts; and the effect is seen still more strikingly in the case of houses which have been submerged in an inundation, which are very unwholesome as long as the wood is moist.

The tendency of wood to decay is checked or destroyed by acids and many salts, especially corrosive sublimate. Out of contact of air, moist wood putrefies, yielding a white friable residue, containing less carbon than the wood. One specimen yielded $C_{10}H_{17}O_{20}$, while the corresponding product of eremacausis above mentioned is $C_{10}H_{15}O_{20}$, and the wood $C_{10}H_{12}O_{20}$.

The composition of brown coal is analogous to that of wood partially decayed, but subjected to changes of the nature of putrefaction, as well as to eremacausis. Two specimens of brown coal yielded $C_{10}H_{11}O_{20}$ and $C_{10}H_{15}O_{20}$.

All the above products of decomposition of wood may be derived from oak wood, $C_{10}H_{12}O_{20}$, by the fixation of oxygen, and the separation of water and carbonic acid.

When the substance called mould, which contains the debris of decayed vegetable matter, is boiled with alcalies, the filtered solution deposits, on the addition of acids, a brown precipitate, which has been called ulmine, humus, humine, geine, ulmic acid, humic acid, and geic acid. It is generally admitted that this precipitate is a product of the action of the alkali on the decayed vegetable matter; and the name of humus, humine, or geine is given to the substance which is believed to yield the humic acid. But this humus has not been isolated, and is not known.

Mulder examined the precipitates obtained from a variety of different sources, decayed wood, turf, peat, mould, &c. With one exception, he found all to contain nitrogen, varying from 2.5 to 7 per cent. It is evident that these substances are vegetable matter in different stages of decay. Mulder considers these precipitates as compounds of water, or water and ammonia, with three different acids: 1. acid of mould, $C_{10}H_{12}O_{14}$; 2. humic acid, $C_{10}H_{12}O_{12}$; 3. ulmic acid, $C_{10}H_{14}O_{12}$.

When sugar is boiled with diluted acids, it yields brown substances analogous to, if not identical with, these acids of Mulder.

It is important to observe the general presence of ammonia in mould, &c. This ammonia has no doubt been absorbed from the air in great part; and this will explain the favorable influence which these substances exert on vegetation. They act also in furnishing, by their slow decay, a continual supply of carbonic acid.

Crenic acid, and apocrenic acid, are two brown extractive matters, analogous to the preceding, and derived from decaying vegetable matter, which are found in certain mineral waters. They both appear to contain nitrogen.

PRODUCTS OF THE DISTILLATION OF WOOD.

When wood is heated in close vessels, it gives rise to an immense variety of products, according to the kind of wood and to the presence or absence of resinous or oily matters. In all cases there are formed gaseous, liquid, and solid products, with a residue of charcoal.

The gases are carbonic acid, carbonic oxide, olefiant gas and marsh gas. The liquids are partly soluble in water, partly insoluble. The latter constitute the tar, and are of a semi-fluid consistence.

The substances soluble in water are, besides water itself, acetic acid, acetone, pyroxilic spirit (hydrate of oxide of methyle), acetate of oxide of methyle, lignone, xylite and mesite.

The oily substances, insoluble in water, are very numerous, including creosote, picamer, eupion, capnomor, &c. Along with these are the compounds which at the ordinary temperature are solid, such as paraffine, naphthaline, cedriret, pittacal, pyrène, chrysène, and pyroxanthine. The last mentioned, being very volatile, chiefly accompanies the acetic or pyroligneous acid.

1. VOLATILE PRODUCTS, SOLUBLE IN WATER.

Acetic acid. — This is one of the chief products of the distillation of woods. Its mode of purification and its properties have been already described. As prepared from this source, it is often called pyroligneous acid. The crude or impure acid is highly antiseptic; not only because vinegar, like most acids, is so, but also because it contains much creosote dissolved. Hence it not only preserves meat, but gives to it a powerful and agreeable smoked flavor.

Pyroxilic spirit. — This name is given to the spirituous liquid, distilled from the crude pyroligneous acid before the latter is purified. It is a mixed fluid, the chief component being hydrated oxide of methyle, which is accompanied by acetate of oxide of methyle, unless it has been rectified with quick-lime, which decomposes the latter. Lignone is the name given to a volatile liquid, somewhat resembling alcohol, observed in pyroxilic spirit by Gmelin and Liebig. Its formula is not ascertained, since it does not, as far as we know, form definite compounds, from which its equivalent might be deduced. Xylite is another similar volatile liquid, which, according to Schweitzer, is $C_{12}H_{12}O_3 = 2(C_2H_5O) + (C_8H_8O_3) = 2MtO + Ac_2O_3$; that is, a compound of 2 eq. oxide of methyle and 1 eq. of a sesquiacetylic acid. When acted on by potash, it yields a crystalline salt, $C_{12}H_{12}O_7, KO$, while hydrated oxide of methyle separates. An excess of potash causes the formation of three products: xylitic naptha, $C_{12}H_{12}O_3$; xylitic oil, C_2H_5O ; and xylitic resin, C_8H_8O . When distilled with sulphuric acid, xylite, if moist, yields a new compound, mesiténe, a volatile liquid, $C_8H_8O_3$. If anhydrous, it yields, besides,

another compound, methol, a less volatile liquid, which appears to be a carbo hydrogen, $C_4 H_2$; isomeric with acetylene, if it be not that radical. Mesite is another volatile ethereal liquid found in pyroxylic spirit, which, according to Schweitzer, is $C_6 H_6 O_2$; isomeric with acetone. He considers it as composed of oxide of methyle and oxide of acetylene, $C_2 H_2 O + C_4 H_2 O = Mt O + Ac O$. The liquid called mesite, by Reichenbach would appear to be acetate of oxide of methyle, $Mt O + Ac O_2$ mixed with a more highly carbonized body, apparently composed of $C_{10} H_{10} O_{10}$. This latter is resolved by the action of lime into 3 eq. acetic acid, $(C_2 H_3 O_2)$, and a volatile liquid, $C_{14} H_{14} O_4$. Along with the above, another liquid appears to occur in the mesite of Reichenbach, the composition of which is $C_{11} H_{11} O_{11}$. In addition to all the liquids above mentioned, as occurring in pyroxylic spirit, acetone is frequently found.

The very great similarity in properties of so many substances, namely, hydrated oxide of methyle, acetate of oxide of methyle, lignone, xylite, mesite, and acetone, is worthy of notice. Most of these liquids have nearly the same density and boiling point; they are all inflammable, and their solubility in water is nearly equal. Hence they all occur mixed, and are with great difficulty separated, so as to obtain each in a state of purity; indeed in most of them we cannot be sure that this has yet been accomplished. It is highly probable, that, like the two first, all the rest will be found to be compounds of methyle. Our knowledge on the subject is still very limited.

The purified pyroxylic spirit, or hydrated oxide of methyle, has been already fully described, along with its chief derivatives.

2. VOLATILE OILY PRODUCTS, INSOLUBLE OR SPARINGLY SOLUBLE IN WATER.

a. *Creosote*, (from *xreas*, flesh, and *σωζω*, I preserve). — This is one of the most important products of the distillation of wood. It is found, partly dissolved, in the pyroligneous acid, partly along with other oils, in the tar. When the crude pyroligneous acid is saturated at 167° with dry sulphate of soda, an oil separates, which contains much creosote. In like manner, by the rectification of tar, an oil of tar is obtained, the heavier portions of which contain a good deal of creosote. These oils are neutralized with carbonate of potash, and the fluid thus deprived of acid is distilled with water. The distilled oil is acted on by diluted phosphoric acid to remove ammonia, and, probably, traces of oily bases, again distilled, and dissolved in aqua potassæ, Sp. G. 1.12, which dissolves the creosote, along with portions of other oils, but separates a good deal of eupion, &c. The alkaline solution is now supersaturated with dilute sulphuric acid, (after having been boiled in the air till it has become dark brown,) when the impure creosote

separates. It is again rectified, and the treatment with potash, boiling, addition of sulphuric acid, and rectification repeated till the rectified oil dissolves entirely in weak potash, and this alkaline solution on being boiled acquires only a slight tinge of color. It is then finally rectified, and is pure when it continues colorless on being kept. The tar of peat appears to be very rich in creosote, and it also occurs in coal-tar. Good tar, from beech wood, is said to contain from 20 to 25 per cent.

Pure creosote is a colorless transparent liquid, of a high refractive and dispersive power of a tolerably fluid but oily consistence. Its Sp. G. is 1.037, according to Reichenbach, its discoverer, and other chemists; but there is some discrepancy on this point, Dr. Christison having always found it as high as 1.060 and upward. Its boiling point is 397° . It gradually becomes colored brown when kept, unless absolutely pure. Creosote has a very strong, peculiar, persistent smell of smoke, analogous also to that of castoreum, not fetid, but unpleasant when concentrated. Its taste is burning, with a sweetish after-taste. It disorganizes the skin, causing a white spot, where the cuticle soon peels off, without inflammation. When applied to the interior of the mouth and to the tongue it smarts strongly, whitening and disorganizing the cuticle.

Internally it is a powerful poison, but in a small dose may be employed advantageously in some cases of vomiting and disease of the mucous membrane. It is given much diluted with water. Externally, it may be employed, either in the form of aqueous solution, of ointment, or pure, as a styptic, and is a valuable application to indolent ulcers, and to many chronic cutaneous affections. Pure creosote, applied to the hollow of a decayed tooth, so as to touch the exposed nerve, instantly relieves, in many cases, the most violent toothache. It acts apparently by coagulating the secretions, and thus forming a covering for the nerve.

Creosote dissolves in about 80 or 100 parts of water, and is exceedingly soluble in alcohol and in acetic acid. These solutions have the smell, taste, and antiseptic power of the creosote.

Creosote possesses a singular antiseptic power. Flesh of all kinds, if steeped for a few hours in a weak solution of creosote, becomes insusceptible of putrefaction; and the same effect is produced when the flesh is exposed to the vapor of creosote. This is the reason why the smoke of wood possesses antiseptic properties: smoked meat or fish is merely meat or fish which has absorbed the vapor of creosote from the smoke in which it has been suspended. The creosote appears to act on flesh, &c., in virtue of its remarkable power of coagulating albumen, which also accounts for its styptic action. Tongues and hams may be smoked and effectually cured by immersing them for 24 hours in a mixture of 1 part of pure creosote and 100 of water or brine; and when thus prepared, they have the delicate smoked flavor observed in reindeer tongues, as usually cured by smoking.

Owing to the difficulty of obtaining creosote quite pure, its composition is hardly ascertained with certainty. According to Deville, whose researches are the most recent, it may be regarded as the alcohol, so to speak, of the series of benzoyle. His analyses lead to the formula $C_{14}H_8O_3 = C_{14}H_7O_2, HO$; but I cannot ascertain whether this be the formula he adopts.

It is particularly to be noticed, that there is a very great resemblance between creosote and carbohic acid (or hydrate of phenyle, C_6H_5O, HO), a substance obtained from coal-tar, and which will soon be described. So great is this resemblance, that I am almost inclined to consider creosote as a somewhat impure carbohic acid. The taste, smell, density, (according to some), boiling point, solubility in water, &c., poisonous and antiseptic action, of these two bodies, are the same. Both combine with alcalies, forming crystallizable compounds, and, what is more important, their composition in 100 parts is almost identical. The chief differences seem to be, that carbohic acid may be obtained in crystals, which, however, on contact with the air instantly liquefy and retain the liquid form, without any appreciable change of composition, apparently from the effect of a trace of moisture. Also, the salts of carbohic acid with bases are more easily formed and more permanent than those of creosote. A splinter or shaving of fir wood, dipped into carbohic acid and then into nitric or muriatic acid, becomes first blue and then brown; which does not appear to be the case with creosote. But Laurent has recently shown, that creosote, when acted on by a mixture of hydrochloric acid and chlorate of potash, yields abundance of chloranile, a character in which it agrees with carbohic acid. Both substances also yield nitropicric acid when acted on by nitric acid, although in the case of creosote this acid is accompanied by others not yet examined. These results I have myself also obtained; and it would appear, that if creosote be not carbohic acid, contaminated with some foreign matter, these two bodies are at least closely connected and belong apparently to the same series, which is either that of benzoyle or that of phenyle. It is not improbable that creosote may be a definite compound of carbohic acid with some substance of closely allied composition, but of basic properties.

Creosote dissolves many organic substances, such as indigo, camphor, fats, essential oils, and resins, and undergoes numerous changes by the action of acids, alcalies, and other reagents, such as chlorine, potassium, and others. With oil of vitriol it is colored purple, and appears to form a coupled acid. None of these reactions or products have been properly investigated, and we shall, therefore, not confuse the reader by a description of them, more especially as the composition of creosote itself is doubtful.

b. *Picamar* is the name given by Reichenbach to another oil discovered by him along with creosote in the heavy oil of tar. It

is purified by a tedious process, by the aid of potash, with which it forms a crystalline compound. When pure, it is a colorless oil, of Sp. G. 1.10, of a burning and very bitter taste (hence its name, from *pix* and *amarus*), and a slight smell. It boils at about 510°. It combines with alkalies, forming crystallizable salts, and may therefore be viewed as an acid in some sense, although it is quite neutral to test paper. Its composition is unknown.

c. Capnomor (from *καπνος*, smoke, and *μορφα*, part), is another oil, discovered by Reichenbach, in the heavy oil of tar, along with creosote and picamar. When the creosote is purified by solution of weak potash, the oil left undissolved contains a good deal of capnomor, which is purified by a tedious process. It is a limpid, colorless oil, of a high refracting power, with an aromatic odor of ginger, and a somewhat styptic after-taste. Its Sp. G. is 0.9775; it is quite neutral, and boils at 365°. With sulphuric acid it is colored red, and yields a coupled acid. Nitric acid converts it into oxalic acid, nitropicric acid, and another crystalline substance not yet examined.

d. Eupion (from *εὔ*, fine, and *πίον*, oil or fat), is a fourth oily liquid, discovered by Reichenbach in oil of tar. Being more volatile than the rest, it is purified chiefly by rectification. When pure it is colorless, very fluid, not greasy to the feel, but less soft than water, tasteless, and of a somewhat agreeable odor, like that of some flowers, such as narcissus. Its Sp. G. is 0.740; and Reichenbach states that he has even obtained it so low as 0.663, being the lightest known liquid. It is volatile, boiling at 117° or lower. It is in the highest degree indifferent, resisting the action of the strongest acids and alkalies. In fact, as it is prepared from the oil of tar by rectification and the action of potash, sulphuric, and nitric acids alternately on the rectified oil, it is evident that it must resist these agents. There is good reason to believe that several, even many, different liquids have been described under this name, and that most of these are not really formed in the tar, but products of the action of acids, &c., on the oil of tar. Reichenbach, however, by simple rectifications of the oil obtained by distilling rape oil, obtained a liquid having the characters of eupion. So much is certain, that similar liquids are formed by the action of oil of vitriol on oil of tar.

The whole of the liquids called eupion are carbohydrogens, and their formula is either CH, or some multiple of this, or else one nearly approaching to such a multiple, as C₈ H₈, &c. It is very remarkable that some of them are very volatile, while others, apparently of the same composition, require a strong heat, from 400° to 500°, for example, to boil them.

The purest varieties of eupion burn with the aid of a wick, yielding a very brilliant luminous white flame, free from smoke, and may hereafter be turned to account.

3. SOLID PRODUCTS OF THE DISTILLATION OF WOOD.

a. Paraffine. — This name is given (from *parum* and *affinis*, because its affinities are feeble) to a white solid volatile substance very similar to wax, discovered by Reichenbach in tar. It occurs in the last portions of the rectification of the tar, which are semi-solid. It is squeezed out, and purified by one or two crystallizations in ether, which dissolves it when boiling, and deposits it on cooling in beautiful silvery scales. These, when melted, assume, on cooling, the aspect of pure white wax.

Paraffine exists in large quantity in the *rangoon petroleum*, and some other bituminous mineral products. It is formed in large quantity in the distillation of wax. It melts at 110° , and distills unchanged at a high temperature. Its Sp. G. is 0.870. It burns, in a wick, with a beautiful clear white light, free from smoke, fully equal to that of the finest wax, if not superior to it. Like eupion, it is highly indifferent, and it is, like eupion, a carbohydrogen, containing either C_2H_4 , or some multiple of it, or a near approach to such a multiple. According to Lewy, it is $\text{C}_{20}\text{H}_{42}$. It is acted on by chlorine with the aid of heat, but the reaction is not yet studied. The strongest acids and alkalies do not act on it, even with the aid of heat, if we except fuming sulphuric acid.

b. Cedriret. — This is another compound discovered by Reichenbach in oil of tar. When impure creosote is dissolved in potash, and acetic acid added, an oil separates, which contains the creosote and other oils; but a certain quantity of oily matter remains dissolved in the acetate of potash. This is distilled, until what passes over causes a red precipitate in a solution of sulphate of iron. It is then collected separately, being pure cedriret. It is a volatile solid, which crystallizes in a solution of sulphate of iron, forming a net-work of orange-red crystals, which dissolve in oil of vitriol with a blue color. Much of the color of oil of tar is probably owing to this substance.

c. Pittacal. — This is yet another compound obtained by Reichenbach from the heavy oil of tar. When the heaviest portions are nearly neutralized by potash, the addition of barytic water gives rise to a deep blue color. This belongs to pittacal, but the mode of its purification is not yet published. When pure, it is a solid, like indigo, of a very fine deep-blue color, exhibiting on the polished surface the aspect of gold. It admits of being fixed on cloth, and would make a valuable dye stuff. Its composition is unknown, but it appears to contain nitrogen. Its name is derived from *πῖττα*, pitch, and *καλός*, beautiful. It is a compound of very great interest, although most probably a product of decomposition of the oil of tar, and not ready formed in it. It is very desirable that it should be further investigated.

d. Pyroxanthine. — This is a volatile crystalline solid, first observed by Scanlan in the crude pyroligneous spirit. When this

is rectified with lime, the lime becomes dark brown; and when this colored mass is acted on by hydrochloric acid, there is left undissolved a dark brown matter, which is a mixture of pyroxanthine and a resinous matter. The mass is boiled with hot alcohol, which, on cooling, deposits the pyroxanthine in crystals, which are purified by recrystallization. They are of an intense yellow color, fusible, and volatile in a current of air, or with the vapor of other substances, but partly decomposed when heated alone in a dry tube. Pyroxanthine dissolves in sulphuric acid with a deep bluish-red, and in strong hydrochloric acid with a splendid purple color, which soon passes to dark brown. I found its composition to be very nearly $C_{21}H_8O_4$; but as it forms no definite compounds, I could not control the analysis.

Such are the chief products of the distillation of wood, as far as they are yet known. Their importance is very great, and will be still greater when they shall have been better studied, as most of them will admit of useful applications. But no doubt can be entertained that the above numerous list is far from being complete, and that more compounds remain to be discovered in tar. Indeed, there is even now good reason to believe that several or most of the substances characterizing coal-tar occur also, although in smaller quantity, in wood-tar. Such substances are naphthaline, anthracene, and others. It is to be borne in mind that the composition of wood-tar varies, according to the kind of wood, the presence or absence of oily or resinous substances, the comparative abundance of nitrogenized matter, and finally the temperature at which the distillation is carried on.

Wood coal, brown coal, or lignite, yields, when distilled, an oil of the consistence of butter, in which creosote, paraffine, and probably eupion, are found, along with other products not yet examined.

PRODUCTS OF THE DISTILLATION OF COAL.

Coal differs from wood in several points, although it is unquestionably derived from the decay, under pressure, of woody fibre and the other substances which make up the mass of the early vegetation of which our coal beds are the remains. Coal contains much less water, and a much larger per centage both of carbon and nitrogen, than wood. Hence it is decomposed at a higher temperature, and yields much ammonia, cyanogen, and other nitrogenized products. We shall not here dwell on ammonia and cyanogen, farther than to mention that out of the aqueous products of the coal gas-works large quantities of ammonia are obtained; and that so much hydrocyanic acid is also present, that a patent was taken out some years since for the preparation of Prussian blue from the gas liquor. We proceed to describe the chief ingredients of coal-tar.

a. Carbolic Acid. *SYN. Hydrated Oxide of Phenyle*, $C_{12}H_5O$, $H O$. — This remarkable acid is found in that portion of the oil of coal-tar which boils between 300° and 400° . This is agitated with twice its volume of potash lye, and the aqueous solution, on the addition of an acid, yields hydrated carbolic acid (impure) as a heavy oil. It is purified by rectification with a very little solid potash.

When pure, carbolic acid generally appears as an oily liquid, colorless, and of a high refracting power, neutral to test paper, of Sp. G. 1.062 to 1.065. It has a burning taste, and the odor of creosote, to which it has a very great resemblance. In certain circumstances it forms long needle-shaped crystals, which very readily lose the solid form by exposure to the atmosphere, and which also liquefy in sealed tubes, without any obvious cause. The crystals melt at 94° , and boil at 368° . The extraordinary resemblance between carbolic acid and creosote has been noticed above; and there can be little doubt that, if not essentially the same, they are closely connected and belong to the same series, or contain the same radical.

A splinter of pine wood, if dipped, first in carbolic acid, and then in moderately strong nitric acid, becomes of a deep blue, which soon passes into brown.

According to Laurent, carbolic acid is the hydrated oxide of phenyle, $C_{12}H_5$, and its formula is $(C_{12}H_5)O$, $H O$. This radical, phenyle, gives rise to a series of derived compounds which may be represented as follows:

Hydrate of phenyle or carbolic acid, .	C_{12}	$H_5, O + H O$
Sulphocarbolic acid (sulphophenic acid),	C_{12}	$H_5, O, H O + 2 S O_2$
Chlorophenesic acid,	C_{12}	$\left\{ \begin{array}{l} H_3 \\ Cl_2 \end{array} \right\} O, H O$
Chlorophenesic acid, identical with the chloridoptenic acid of Erdmann,	C_{12}	$\left\{ \begin{array}{l} H_2 \\ Cl_2 \end{array} \right\} O, H O$
Chlorophenesic acid, chlorinized chlo- rindoptenic acid of Erdmann,	C_{12}	$\left\{ \begin{array}{l} Cl_3 \\ Cl_3 \end{array} \right\} O, H O$
Bromophenesic acid,	C_{12}	$\left\{ \begin{array}{l} H_2 \\ Br_2 \end{array} \right\} O, H O$
Nitrophenesic acid,	C_{12}	$\left\{ \begin{array}{l} H_3 \\ 2 N O_4 \end{array} \right\} O, H O$
Nitrophenesic acid, identical with ni- tropic acid,	C_{12}	$\left\{ \begin{array}{l} H_2 \\ 3 N O_4 \end{array} \right\} O, H O$
Phenylamide (aniline),	$C_{12}H_5$	Ad.

Thus the carbolic acid is connected with the derivatives of indigo, of salicyle, and other bodies, which yield nitropic acid. This connection is also shown in the formation of chloranile, from carbolic acid, by the action of chlorate of potash and hydrochloric acid. (See under Indigo, the formation of chloranile from aniline). It is also shown by the fact, that salicylic acid, $C_{14}H_5O_6$, when distilled alone, with lime, or with pounded glass, is resolved into

carbonic acid, 2C O_2 , and carbolic acid, $\text{C}_{12} \text{H}_8 \text{O}_2$. The action of carbolic acid, on organic compounds, is the same as that of creosote. Thus it dissolves indigo, &c., and coagulates albumen, preventing the putrefaction of animal substances.

With bases it forms salts, some of which crystallize, but which retain an alkaline reaction. With oil of vitriol, it yields a coupled acid, sulphocarbolic, or sulphophenic acid, which forms a soluble salt with baryta.

The formulæ in the above table illustrate the formation, by substitution, of the chlorophenesic, chlorophenistic, and chlorophenusic, of the nitrophenesic and nitrophenistic acids. It is not necessary here to do more than point out their relation to carbolic acid and phenyle. The chlorobenzide of Mitscherlich, $\text{C}_{12} \text{H}_8 \text{Cl}_2$, is, according to Laurent, hydrochlorate of chlorophenise, $3 \text{H Cl} + \text{C}_{12}$

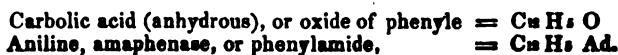
$\left\{ \begin{array}{l} \text{H}_8 \\ \text{Cl}_2 \end{array} \right.$. This last body, chlorophenise, which is obtained by the action of potash on chlorobenzide, would appear to be derived by substitution, not from phenyle $\text{C}_{12} \text{H}_8$, but from benzole $\text{C}_{12} \text{H}_6$; although it may be derived also from oxide of phenyle $\text{C}_{12} \left\{ \begin{array}{l} \text{H}_8 \\ \text{O} \end{array} \right.$; as may benzole itself. Chlorophenise cannot be obtained directly from hydrate of phenyle, or its derivatives; but, on the other hand, the series of benzole has an obvious relation to that of phenyle. In fact, Laurent considers benzole as in some measure the fundamental compound, or nucleus, and calls it phene = $\text{C}_{12} \text{H}_6$.

It has already been stated that nitrophenistic acid is identical with nitropicric acid. Nitrophenesic acid is somewhat similar, and forms salts which crystallize with facility, and detonate when heated. The nitrophenesate of baryta is a beautiful salt, like bichromate of potash.

b. Volatile Bases of Coal-Tar.

Besides carbolic acid, Runge found in coal-tar two other acids, rosolic and brunolic acids (of which little is known), and three basic volatile oils, kyanol, leukol, and pyrrol. The last has been little examined; but the recent researches of Hoffman have confirmed Runge's statements as to the two first, which have also been identified with bases produced from different quarters, namely, aniline and quinoline or leucoline. These bases have already been fully described under the head of volatile artificial alcaloids.

That there is a relation between aniline and carbolic acid appears from their formulæ; for aniline is the amidide of carbolic acid, or phenamide, being thus deduced from carbolate of ammonia: $\text{C}_{12} \text{H}_8 \text{O}, \text{N H}_2 = \text{H O} + \text{C}_{12} \text{H}_8, \text{N O}_2$. The relation may be better exhibited thus:



As another experimental proof of this relation, it may be mentioned that salicylamide, $C_{14}H_9O_4, N H_2 = C_{14}H_7 N O_4$, which has the same composition as protonitrobenzoene and anthranilic acid, both of which yield aniline, when heated with lime, gives not aniline but carbolic acid, ammonia, and probably a carbohydrogen.

It will be remembered that picoline is isomeric with aniline. Adopting Laurent's nomenclature, as explained under naphthaline both these compounds would be called amaphenase; and the relation between them would be the same as between any two of the seven forms of chlonaphtese; that is, in aniline the particular molecule of hydrogen, replaced by amide, is different from the molecule replaced in picoline. Aniline, therefore, would be amaphenase *a*, and picoline amaphenase *b*. For the explanation of the views entertained on this and similar subjects, see *Chlonaphtase*.

Of pyrrol, and of rosolic and brunolic acids, so little is known that we need not dwell on them.

c. Volatile Carbohydrogens in Coal-Tar.

a. Naphthaline, $C_{10}H_8$, or $C_{20}H_{12}$.—This remarkable compound occurs in all kinds of tar, but most abundantly in coal-tar, as being formed at a very high temperature. It is formed in additional quantity when any of the elements of oil of tar, such as creosote, carbolic acid, &c., or even alcohol and ether, are passed through tubes heated to a strong red-heat. It is easily obtained by redistilling coal-tar, when the latter portions are so full of naphthaline as to be semi-solid. It is well squeezed out, and purified by sublimation and crystallization in hot alcohol. Or the oil of coal-tar, is saturated with chlorine gas, which, by destroying some of the oils, allows the naphthaline to crystallize.

Pure naphthaline is colorless and volatile, and forms large tabular transparent crystals of a very peculiar smell, and an acrid aromatic taste. It boils at 414° , but distils easily with the vapors of water, and is dissipated, like camphor, if left exposed at the ordinary temperature.

It is acted on by chlorine and bromine, which combine with it in the first instance, and also give rise to a large number of compounds formed by substitution; and by sulphuric and nitric acids, each of which produces a number of new compounds with it. These changes have been studied with singular perseverance and remarkable sagacity, by Laurent, more especially the action of chlorine, bromine and nitric acid. His researches have been attended with unusual success, and he may be said to have originated and established, by these researches, the new received doctrine of substitutions. I cannot hope to give even an accurate outline of all that Laurent has done in this department, because I have nowhere seen a complete account of these curious results as they now

stand ; but until the author himself shall publish a complete account of his researches on naphthaline, I shall place before the reader such a general account of them as may show the great importance of the subject, and some of the interesting facts already ascertained.

1. ACTION OF CHLORINE AND BROMINE ON NAPHTHALINE.

[It is necessary here to explain the principle of nomenclature, provisionally adopted by Laurent, especially for cases like this of substitutions, where the ordinary nomenclature is entirely inapplicable. The nomenclature of Laurent may be thought, by some, uncouth ; but it is simple, systematic, and consistent with itself. Beginning with naphthaline, he gives to the compounds formed by the successive substitution of chlorine for hydrogen, names beginning with *chlo*, and ending with a syllable in which the vowels *a*, *e*, *i*, *o*, and *u*, are employed to designate the replacement of 1, 2, 3, 4 and 5 eq. of hydrogen. Thus, if in naphthaline, $C_{10}H_8$, 1 eq. of hydrogen is replaced by chlorine, we have the compound $C_{10} \begin{Bmatrix} H_7 \\ Cl \end{Bmatrix}$. This is called *chlonaptase*. The compound $C_{10} \begin{Bmatrix} H_6 \\ Cl_2 \end{Bmatrix}$ is *chlonaptose*; $C_{10} \begin{Bmatrix} H_5 \\ Cl_3 \end{Bmatrix}$ is *chlonaptise*, &c. The corresponding compounds of bromine are *bronaptase*, *bronaptese*, and *bronaptise*. When we get as far as *chlonaptuse*, $C_{10} \begin{Bmatrix} H_3 \\ Cl_5 \end{Bmatrix}$, as there are no more vowels, we begin with *a*, adding a syllable to the word. Thus, $C_{10} \begin{Bmatrix} H_2 \\ Cl_6 \end{Bmatrix}$ is *chlonaptalase*, $C_{10} \begin{Bmatrix} H \\ Cl_7 \end{Bmatrix}$ is *chlonaptalese*, and $C_{10} \begin{Bmatrix} H_0 \\ Cl_8 \end{Bmatrix}$ is *chlonaptalise*, and so on with bromine. When hydrogen is replaced, partly by chlorine, partly by bromine, then the name is so constructed that the final syllable indicates the sum of the equivalents of chlorine and bromine, while both chlorine and bromine are prefixed. Thus, *chlonaptose* is $C_{10} \begin{Bmatrix} H_4 \\ Cl_4 \end{Bmatrix}$; and the compound $C_{10} \begin{Bmatrix} H_4 \\ Cl_3 \\ Br \end{Bmatrix}$ is *chloribronaptose*; $C_{10} \begin{Bmatrix} H_4 \\ Cl \\ Br_3 \end{Bmatrix}$ is *chlorabronaptose*. The former of these two may also be *bromachlonaptose*, and the latter, *bromichlonaptose*. We shall see hereafter that it may be necessary to use both forms to distinguish different compounds which are isomeric. Again, where hydrogen is replaced by NO , we have, (NO being represented by X), $C_{10} \begin{Bmatrix} H_7 \\ X \end{Bmatrix}$ *nitronaptase*, and so forth. In like manner, if H were replaced by Ad ($Ad = NH_2$), we should have $C_{10} \begin{Bmatrix} H_7 \\ Ad \end{Bmatrix} = C_{10}H_6$. N . This would be called *amanaptase*; and such a compound has been already described under the name of naphthalidine. It is evident that this nomenclature, although it gives rise to words

of a singular aspect, is yet easily understood, and may even, in many cases, serve as well as a formula to remind us of the composition. Laurent has applied it to many other series, as we have seen in the series of phenyle, where we have chlorophenesic, chlorophenetic, and chlorophenetic acids, &c.]

When chlorine is brought in contact with naphthaline, the latter melts, and there are formed at once two compounds of chlorine and naphthaline; the chloride of naphthaline, $C_{10}H_8 + Cl_4$; and the subchloride of naphthaline $C_{10}H_8 + Cl_2$. At the same time hydrochloric acid is disengaged, arising from the action of chlorine on one of these chlorides. The former is a solid, which is best purified by solution in hot oil of petroleum, which deposits it on cooling in crystals. It may also be purified by means of boiling ether, which dissolves it to a certain extent and deposits it on cooling. Chloride of N is decomposed by heat, yielding no less than four different isomeric forms of chlonaphtese. An alcoholic solution of potash converts it into two more forms of chlonaphtese. It is also acted on by chlorine, bromine, nitric acid, and sulphide of ammonium, yielding many new compounds.

Subchloride of N is an oily liquid, which by the action of heat is partially changed into hydrochloric acid, and one form of chlonaphtese. An alcoholic solution of potash also converts it into chlonaphtese and chloride of potassium. Chlorine converts it into two chlorides of chlonaphtese, isomeric but distinct; if the heat is too strong there is formed one kind of chlonaphtise.

When bromine is made to act on naphthaline, no bromide of N is formed, but hydrobromic acid is separated and bronaphtase is produced.

Chlonaphtase, $C_{10}(H_7 Cl)$, is obtained by acting on subchloride of N by alcoholic solution of potash. On the addition of water, an oily liquid separates, which is purified by rectification, and is then chlonaphtase. No isomeric modification of it is yet known, but the existence of such is extremely probable. Bromine acts on it, converting it into bromide of chlorabronaphtese, $Br_4 + C_{10}H_8 Cl Br$.

Bronaphtase, $C_{10}(H_7 Br)$, is formed by the direct action of bromine on naphthaline, care being taken to avoid excess of bromine, which would form bronaphtese, and excess of naphthaline, which would remain unchanged. Bronaphtase is a colorless oil, decomposed by chlorine and bromine, the latter converting it into bronaphtese and the products of the further action of bromine on bronaphtese. As yet only one form of bronaphtase is known.

Chlonaphtese, $C_{10}(H_8 Cl_2)$, occurs in no less than seven different isomeric forms. These are distinguished by Laurent as modifications *a*, *c*, *ad*, *e*, *f*, *x*, and *y*, but I am not aware of the principle on which these letters are selected. *a*, *c*, *f*, and *x*, are obtained by the action of heat on the chloride of N; *ad* and *e* by boiling chloride of N with tincture of potash; and *y* by the action

of chlorine on nitronaphtese. α and x are liquid, all the rest crystallize easily. The solid forms have each a different point of fusion, and the whole seven give different results when acted on by chlorine and bromine. Since, therefore, the composition of all seven is the same, we are compelled to adopt the conclusion that it is not the same 2 eq. of hydrogen which are replaced by chlorine, and that it is not indifferent which equivalents of hydrogen are thus replaced, but that, on the contrary, the properties of these compounds depend on the particular equivalents or molecules of hydrogen replaced by chlorine, and that consequently the arrangement, or relative as well as absolute position of these molecules in the compound molecule, is a matter of far greater importance (at least, in this and other analogous cases), in reference to chemical characters, than the properties of the elements, or their place in the electrochemical arrangement.

Referring to what I have said on the subject of types, at pp. 260-265, I would here point out that naphthaline is a type, the molecule of which is made up of 20 equivalents (not single atoms, but molecules) of carbon, and 8 equivalent molecules of hydrogen; and that chlonaphtese is a subtype, in which the 20 molecules of carbon are associated, as in the fundamental type, with 8 other molecules, not all, as before, of hydrogen, but 6 of hydrogen and 2 of chlorine, a body usually considered as entirely opposed to hydrogen, chlorine being strongly negative, and hydrogen strongly positive. Yet the type remains unchanged, and we cannot help seeing that the 2 molecules of chlorine, *in virtue of their position in reference to the 20 of carbon*, are playing the part of 2 molecules of hydrogen.

Farther, if we conceive the 8 molecules of hydrogen in the fundamental type to occupy each a fixed position, in relation to the 20 of carbon, we see from the wonderful phenomena just indicated, namely, from the existence of seven distinct forms of chlonaphtese, that, in each of these, a different pair of molecules of hydrogen has been replaced by chlorine. If the 8 molecules of hydrogen be supposed to be numbered, according to the fixed position of each in the compound molecule of the type, then we can see that in chlonaphtese α , the molecules 1 and 2 may be those replaced, while in c the molecules 6 and 7 may be those replaced by chlorine, and so on. It is easy to calculate that in this way at least 28 different isomeric forms of chlonaphtese may exist, and of these seven are already known.

Our space will not admit of details on the different forms of chlonaphtese, but I have thought it indispensable to explain the view now taken of these singular compounds, in a general way. It is evident that we may expect much light to be thrown on the obscure subject of the molecular arrangement of compounds by continued researches in the same direction. The recent progress

of those departments of physics which are most closely allied to chemistry, has established the existence of certain relations between the atomic weight and constitution of compounds and their physical properties, such as volume or density, volatility, state in regard to cohesion, solidity, fluidity, &c., and crystalline form. We now see a prospect of tracing the connection between the molecular arrangement of compound bodies and their chemical properties; and we may even hope hereafter to be enabled, simply by accurate observation of the external properties of a body, physical and chemical, to ascertain its composition and constitution; and also to predict with accuracy the properties of compounds yet unformed, the formation of which will probably become a problem, solvable by a few rules of universal application.

For the present, we have only the distant prospect of these results; but we have only assiduously to pursue the study of nature on true inductive principles, in order to be hereafter enabled to bring into order the chaos, so to speak, of interesting and important observations, the number of which is hourly increasing, while a large proportion of them have not yet found a use or an application. We must now return to the derivations of naphthaline, which we have only space briefly to name.

Bronaphtese, $C_{10}(H_2 Br_2)$, is easily formed by the action of bromine on naphthaline or on bronaphtase. It is a crystallizable solid, and probably corresponds to chlonaphtese *c*. Only one bronaphtese is yet known. It forms several compounds with bromine.

Chlonaphtise, $C_{10}(H_2 Cl_2)$, occurs in six different forms (out of 55 which are possible), *a*, *ac*, *c*, *g*, *d*, and *ad*, all of which are crystallizable solids. They are obtained in different ways: *a* by boiling with tincture of potash the oily modification of chloride of chlonaphtase; *ac* by the action of chlorine on chlonaphtese *ad*, melted; and *g* along with some of *a*, by boiling with tincture of potash the crystallized chloride of chlonaphtase; *d* by distilling the crystallized chloride of chlonaphtase; and *ad* by boiling with tincture of potash the double chloride of naphthaline and of chlonaphtase; *a* is converted by chlorine into chlonaphtose *a*; and bromine converts it into chloribronaphtose *a*.

Bronaphtise, $C_{10}(H_2 Cl_2)$, is obtained by heating the bromide of bronaphtise, when bromine is given off. It is crystallizable. Only one form is yet known.

Chlonaphtose, $C_{10}(H_4 Cl_4)$, occurs in four isomeric forms, *a*, *b*, *c*, and *k*, out of a very large number which are possible. They are all crystallizable. It is unnecessary to mention the methods employed to obtain them, which are analogous to those already described for chlonaphtise or chlonaphtese.

Bronaphtose, $C_{10}(H_4 Br_4)$, appears to exist in two forms, *a* and *b*, both crystallizable.

Chlonaphtuse, $C_{20}(H_3 Cl_3)$, and bronaphtuse, $C_{20}(H_3 Br_3)$, are not yet known.

Chlonaphtalase, $C_{20}(H_2 Cl_4)$, is obtained by the action of chlorine on chlonaphtise α . It forms soft flexible prisms.

Chlonaphtalese, $C_{20}(H Cl_7)$, is not yet known.

Chlonaphtalise, $C_{20}Cl_8$, the compound in which all the hydrogen of naphthaline is replaced by chlorine, is obtained by continuing the action of chlorine on chlonaphtise α . It is also crystallizable. Laurent, apparently from its crystalline form, considers it to correspond with the modifications c of chlonaphtese and chlonaphtise; and for the same reason he considers the only chlonaphtalase known, as chlonaphtalase α . In the case of chlonaphtalise, if different modifications can occur, they must depend on a different principle from that which regulates the modifications of those compounds in which both chlorine and hydrogen are concerned.

But until Laurent shall publish a complete account of his views, it is not easy to ascertain exactly what those views are. I suspect some error in the only account of these researches to which I could refer.

Besides the above, there are a number of compounds derived from naphthaline, in which the hydrogen is replaced by bromine and chlorine at once.

Chlorebronaphtise α , $C_{20}(H_3 Cl_2 Br)$, is a crystalline solid very similar to chlonaphtise α .

Chlorebronaphtose b , $C_{20}(H_4 Cl_2 Br_2)$, is obtained by the action of bromine on chlonaphtese f .

Chloribronaphtose α , bromachlonaphtose α , and bromachlonaphtose b , are three isomeric compounds. The first is obtained by the action of bromine on chlonaphtise α , and the bromine is, therefore, placed second in the name. The two others are both formed when chlorine acts on bronaphtese. These are the compounds alluded to at p. 265. They furnish a very beautiful proof of the truth that the position of the replaced or replacing molecule is all-important. They are all crystallizable.

Bromechlonaphtose b , $C_{20}(H_3 Cl_3 Br_2)$, is a crystalline solid obtained by boiling chloride of bromechlonaphtise with tincture of potash.

Chloribronaphtuse, $C_{20}(H_3 Cl_3 Br_2)$, is a crystalline solid, formed by the action of bromine on chloride of naphthaline.

There remain to be described some compounds, analogous to the chlorides of naphthaline, and containing consequently chlorine or bromine, in addition to the type or subtype.

Chloride of chlonaphtase, $Cl_4 + C_{20}(H_7 Cl)$, is obtained by the action of chlorine on the subchloride of naphthaline. It is the most remarkable of the whole series from the great size and beauty of its crystals. It occurs in an isomeric form as an oily

liquid. When distilled, these compounds yield different forms of chlonaphtise mixed together.

Chloride of chlonaphtese, $\text{Cl}_4 + \text{C}_{20}(\text{H}_5 \text{Cl}_2)$, occurs in three isomeric forms. *a* and *x* are oily liquids, derived respectively from chlonaphtese *a* and *x* by the action of chlorine. *c* is derived from chlonaphtese *c* in the same way, and is crystalline. They all yield chlonaphtose when heated, but in different forms.

Bromide of chlonaphtese, $\text{Br}_4 + \text{C}_{20}(\text{H}_5 \text{Br}_2)$, is obtained by the action of bromine on chlonaphtese *c*. It is crystalline. An excess of bromine produces at least five different compounds.

Bromide of chlorabronaphtese, $\text{Br}_4 + \text{C}_{20}(\text{H}_5 \text{Br Cl})$, is formed when bromine acts on chlonaphtase. It is crystalline.

Bromide of bronaphtese, $\text{Br}_4 + \text{C}_{20}(\text{H}_5 \text{Br}_2)$, is formed by the action of bromine on bronaphtese. It is crystalline, and when distilled yields hydrobromic acid and bronaphtose.

Subbromide of bronaphtise, $\text{Br}_2 + \text{C}_{20}(\text{H}_5 \text{Br}_2)$, is formed along with the preceding. It is also crystalline.

Bromide of bronaphtise, $\text{Br}_4 + \text{C}_{20}(\text{H}_5 \text{Br}_2)$, is also a highly crystalline solid.

Subchloride of bronaphtase, $\text{Cl}_2 + \text{C}_{20}(\text{H}_7 \text{Br})$, formed by the action of chlorine on bronaphtase, crystallizes in regular rhomboidal plates.

Chloride of bronaphtese, $\text{Cl}_2 + \text{C}_{20}(\text{H}_5 \text{Br}_2)$, crystallizes in long prisms. Perchloride of bronaphtise, $\text{Cl}_4 + \text{C}_{20}(\text{H}_5 \text{Br}_2)$, crystallizes in right prisms with rhombic base.

Chloride of bromechlonaftise, $\text{Cl}_4 + \text{C}_{20}(\text{H}_5 \text{Br}_2 \text{Cl})$, crystallizes in oblique rhombic prisms. When boiled with tincture of potash it yields bromechlonaftuse, $\text{C}_{20}(\text{H}_5 \text{Br}_2 \text{Cl}_2)$.

All the preceding compounds have been discovered, studied, analyzed, and described by Laurent, besides a large additional number of derivatives of naphthaline, under the agency of chlorine and bromine, which he has not so fully examined. Those here named are sufficient to illustrate the endless variety of compounds attainable. Every subtype of the original type of naphthaline admits of numerous permutations, and where both chlorine and bromine are present, the number of possible permutations is enormously increased. In short, these remarkable researches have only made us acquainted with a very small selection of the possible products of the action of chlorine and bromine on naphthaline, the type remaining unchanged.

Thus the subtype chlonaphtose, $\text{C}_{20}(\text{H}_4 \text{Cl}_4)$, admits of 65 isomeric modifications, all different, as does of course bronaphtose also. But these subtypes may yield the modified subtypes, chlorabronaphtose, chorebronaphtose, chloribronaphtose, bromachlonaphtose, bromechlonaftose, and bromichlonaphtose, and others, difficult to name, depending on the relative proportions and positions, in the molecule of the subtype, of the 4 eq. chlorine and

bromine. It is easy to imagine 14 such modified subtypes, and there appears no reason why each of them, with the two subtypes, should not admit of at least 65 isomeric forms. This would give 1040 isomeric forms, all included under the two subtypes chloronaphtose and bronaphtose, or under one subtype which may be called naphtose, $C_{20}(H_4 X_4)$. X is here put for chlorine or bromine.

2. ACTION OF SULPHURIC ACID ON NAPHTHALINE.

When naphthaline is dissolved in warm oil of vitriol to saturation, the solution, if left exposed to the air, becomes a semi-solid mass of a dirty purplish color. This, dried on a porous brick, leaves a quantity of scales, very soluble in water and alcohol, which are a mixture of two acids.

a. *Hyposulphonaphthalic Acid*, $C_{20}H_8S_2O_5 + H_2O$?—The above mixture, being dissolved in water, is saturated with carbonate of lead, which forms insoluble sulphate of lead, and two soluble salts, one of which is soluble in alcohol and contains this acid, and yields it when decomposed by sulphuretted hydrogen. The acid forms a hard crystalline fusible mass of an acid and bitter taste. Its salts are soluble and crystallizable. Their formula is $C_{20}H_8S_2O_5, MO$.

b. *Hyposulphonaphtic Acid*, $C_{11}H_5S_2O_5 = C_{11}H_4S_2O_5, H_2O$? The lead salt insoluble in alcohol contains this acid, the salts of which are soluble, bitter, and hardly crystallizable. It is possible that a third acid accompanies these two: for Faraday obtained a third salt of baryta, and Berzelius found a third salt of lead in the mother liquid of the other two. Faraday's salt, which remains with the sulphate of baryta formed in the process by the free sulphuric acid, and may be extracted by boiling water, yields about 42 per cent. of sulphate of baryta when calcined.

The vapors of anhydrous sulphuric acid, passed over fused naphthaline, form with it a red liquid. If the acid be in excess, there is formed a new acid, the hypsulphoglutinic acid, besides small quantities of the preceding acids; if there be excess of naphthaline there are formed two neutral bodies, sulphonaphthaline and sulphonaphthalide.

Hypsulphoglutinic acid, when pure and dry, is a hard glassy mass. When precipitated from its salts by stronger acids, it forms a viscid hydrate like turpentine. Its salts are generally soluble and do not crystallize. Its composition is unknown.

Sulphonaphthaline, $C_{20}H_8SO_2$? is a crystalline fusible solid.

Sulphonaphthalide, $C_{20}H_{10}SO_2$? is a crystalline powder not fusible at 212° .

3. ACTION OF NITRIC ACID ON NAPHTHALINE, AND ITS DERIVATIVES.

Nitric acid acts on naphthaline, and gives rise to a whole series of compounds in which NO_2 is substituted for hydrogen. The

same principles apply here as in the action of chlorine and bromine on naphthalene. It is to Laurent that we are indebted for our knowledge of these compounds, which our space will only allow us to name.

Nitronaphtase, $C_{20}H_7X$, (X is here put for NO_4), is best formed by causing nitrous acid to pass through melted naphthalene. It is purified by means of alcohol, and forms long prisms of a sulphur-yellow color, fusible at 110° . Chlorine decomposes it, producing chlonaphtose. Nitric acid converts it into nitronaphtese. By the action of sulphuretted hydrogen and ammonia it yields, as has been already explained, a base, naphthalidine or amanaphtase, $C_{20}AdH_7 = C_{20}H_5N$.

Naphtalase, $C_{20}(H_7O)$, is a yellow crystalline solid formed by gently heating nitronaphtase with 10 parts of lime slightly moistened. It communicates to oil of vitriol a magnificent blue color. It is insoluble in alcohol as well as in water, otherwise it would recall pyroxanthine, which is yellow and volatile and colors sulphuric acid purple.

Nitronaphtese, $C_{20}(H_5X_2)$, forms a crystalline powder fusible at 365° , insoluble in water, very sparingly soluble in alcohol. It is converted, by the action of sulphuretted hydrogen and ammonia into the new artificial base, seminaphthalidine, $= C_{10}H_5N$.

Nitronaphteise, $C_{20}(H_{5\frac{1}{2}}X_{2\frac{1}{2}})$? is a crystalline compound formed when naphthalene is added in small quantities to a large mass of hot nitric acid. Nitronaphtese is produced along with it. It is pale yellow and very fusible, becoming liquid even in boiling alcohol. This great fusibility prevents us, notwithstanding its strange formula, from considering it as a mixture of nitronaphtese and nitronaphtise, the former of which melts at 365° , the latter at 410° , and which are very insoluble in ether, in which liquid nitronaphteise readily dissolves.

Nitronaphtise, $C_{20}(H_5X_3)$, is formed along with the preceding, and crystallizes in rhomboidal plates of a pale yellow color, fusible at 410° .

Nitronaphtale, $C_{16}H_5N_3O_{11}$, is a crystalline substance, formed by the long-continued action of nitric acid on the mother liquor of all the preceding. It melts at 420° , and sometimes solidifies in an amorphous state; a slight heat, or touching the melted substance with a point, causes it to crystallize.

Nitronaphtesic acid, $C_{16}H_4\frac{1}{2}N_1\frac{1}{2}O_4$? $C_{32}H_5N_3O_8$? — This acid is formed when nitronaphtalese is boiled with tincture of potash, and is separated from the potash by nitric acid. When dry it is brownish-black, and forms brown salts, which are soluble and uncrystallizable. Nitronaphtalésic acid, $C_{12}H_1O_6N_1\frac{1}{2}$, or $C_{24}H_2O_{12}N_3$, is a similar acid, formed from nitronaphtaléise. Nitronaphtisic acid, is another brown acid, formed in the same way from nitronaphtalise.

Oxide of chloroxénaphthosé, $O_2 + C_{20}(H_4 Cl_2 O_2)$, is formed when nitric acid acts on crystallized chloride of chlonaphthosé. It appears as a yellow crystalline solid. It is accompanied by chloranaphthisic acid, into which it is also converted by boiling with tincture of potash.

Chloranaphthisic acid, $C_{20}H_4ClO_2$, is formed from the preceding compound, as follows: $C_{20}H_4Cl_2O_2 + H_2O + 2KO = KCl + (C_{20}H_4ClO_2 + KO)$. It is separated from the potash by adding an acid, and forms yellow crystals, fusible at 392° . Its salts are for the most part insoluble, and exhibit the most beautiful colors, including yellow, orange, red, and carmine.

Oxide of chloroxénaphthalise, $O_2 + C_{20}Cl_2O_2$, is obtained along with chlorphtalisic acid and other compounds, when nitric acid is boiled with chlonaphtalase, $C_{20}H_2Cl_2$. It forms golden scales.

Chloroxénaphthalésic acid, $C_{20}HCl_3O_2$, is formed when the preceding compound is acted on by potash, which at once changes it into a fine carmine-red substance, from which acids separate the new acid as a yellow crystalline powder. It forms beautiful red salts with potash and ammonia. It is formed as follows: $C_{20}Cl_2O_2 + H_2O + 2KO = (C_{20}HCl_3O_2 + KO) + KCl$.

Phtalic or naphthalic acid, $C_{10}H_4O_2$, $2H_2O = C_{10}H_2O_2$, is formed by the action of nitric acid on chloride of naphthaline. It forms rounded groups of lamellar crystals, and yields crystallizable salts. When distilled with lime it yields benzole (phéne), and carbonic acid, $C_{10}H_2O_2 = 4CO_2 + C_{10}H_2$. When the hydrated acid is distilled, it yields the anhydrous acid in fine elastic needles.

The acid phtalate of ammonia, $C_{10}H_4O_2, NH_4O, H_2O$, when heated, yields water, $4H_2O$, and phtalimide, $C_{10}H_2NO_2$.

Phtalamide, $C_{10}H_2NO_2$, is obtained by acting on anhydrous phtalic acid by ammonia. It appears that phtalimide is acid phtalate of ammonia, minus 4 eq. water, while phtalamide is anhydrous phtalate of ammonia, $C_{10}H_4O_2 + NH_3$, minus 1 eq. water. Both are crystalline solids, and both appear to form definite compounds with oxide of silver.

Nitrophtalic acid, $C_{10}H_3NO_4, 2H_2O$, is derived from phtalic acid by the substitution of 1 eq. NO_2 for 1 eq. hydrogen: $C_{10}H_4O_2 - H + NO_2 = C_{10}H_3NO_4$. It forms beautiful pale yellow crystals; and when gently heated, it yields the anhydrous acid in fine white needles.

Chlorphtalisic acid, $C_{10}HCl_3O_2$, is formed along with the oxide of chloroxénaphthosé when chlonaphtalase is boiled with nitric acid. It is crystallizable, and represents anhydrous phtalic acid, in which 3 eq. hydrogen have been replaced by 3 eq. chlorine.

To judge from the action of chlorine unaided by heat, and of nitric acid, on naphthaline, that body, $C_{20}H_{12}$, is composed of two carbohydrogens, $C_{10}H_4$ and C_4H_4 , the latter of which is more

easily altered. The former, plus 6 eq. oxygen, yields phthalic acid, $C_8H_4 + O_6$; and the substitution in phthalic acid of $N O_4 (= X)$, for H yields nitrophthalic acid, $C_8 \begin{cases} H_3 \\ X + O_6 \end{cases}$.

β. *Anthracene*, $C_{30}H_{12}$. — This compound, which is polymeric with naphthaline, is also found in coal-tar, and is sometimes called paranaphthaline. It melts at 356° , and distils at 392° , yielding foliated plates. When acted on by nitric acid, it gives rise to a series of compounds, in which oxygen is substituted for hydrogen, while the compounds thus formed combine with hyponitrous acid. Thus we have,

Anthracene	$C_{30}H_{12}$
Hyponitrite of anthracenase . . .	$C_{30}H_{11}O + N O_3$
Bi-hyponitrite of anthracenase . .	$C_{30}H_{10}O_2 + 2 N O_3$
Ter-hyponitrite of anthracenase . .	$C_{30}H_9O_3 + 3 N O_3 + 3 H O$
Hyponitrite of anthracenose . . .	$C_{30}H_8O_4 + N O_3$
Hyponitrite of anthracenuse . . .	$C_{30}H_7O_5 + N O_3 + H O$
Anthracenuse	$C_{30}H_7O_5$
Chloranthracenese	$C_{30}H_{10}Cl_2$

The second compound of the above list is not known; but its existence is probable. In all the works to which I have access, there appear to be errors, probably of the press, in the table, which I have ventured to correct, so as to bring the formulæ into correspondence with the systematic names devised by Laurent, who discovered all these substances, on the same principle as in the case of naphthaline.

γ. *Chrysenes*, C_3H , or $C_{12}H_4$, is found among the last portions of the rectification of coal-tar. It is a yellow crystalline solid, insoluble in most liquids. It melts at 455° .

δ. *Pyrene*, $C_{10}H_2$, or $C_{15}H_2$, is found accompanying the preceding. It is a good deal more fusible. When acted on by nitric acid both of the above compounds yield modifications, called, by Laurent, the hyponitrites of chrysenase and of pyrenase, $C_{12}H_3O + N O_3$, and $C_{15}H_2O + N O_3$. The former, by the continued action of nitric acid, is converted into $C_{12}H_3O_3 + 2 N O_3$, which Laurent calls nitrite of chrysenese (properly, of chrysenase?).

When bituminous shale is distilled, it yields a thick empyreumatic oil, composed of several products. Among these is an oil apparently identical with eupion, and another very peculiar oil, called ampeline. This oil has neither taste nor smell, but is in some points more analogous to creosote than to any other substance. It dissolves in water, but a few drops of acid cause it to separate. Its composition is still unknown. It may possibly be a product of the action of oil of vitriol, which is used in its preparation, on some other substance.

Ampelic Acid is formed by the action of nitric acid on that part of the oil of schist which distils at 300° . It is oily, soluble in

hot water, and forms very soluble salts. Its composition is not known with certainty. A similar oil, obtained from coal-tar, was found to contain $C_{14}H_8O_2$. This would be isomeric with hydrated salicylic acid.

FOSSIL RESINS, WAX, OIL, NAPHTHA, ETC.

Retinite or retinasphalt is a fossil resin found in lignite or wood-coal. It is fusible and combustible, and almost entirely soluble in alcohol. Retinic acid, $C_{21}H_8O_3$, was found by Johnston in the retinasphalt of Bovey.

Hatchetine is another fossil resin found in the lignites of Wales. It is colorless, or slightly yellow, fusible and volatile.

Scheererite is a colorless, translucent substance, of a pearly lustre, found in the Swiss lignites. Both hatchetine and scheererite appear to be carbohydrogens, and much resemble paraffine, not quite pure.

Middletonite is a fossil resin, found, near Leeds, in coal.

Idrialine is a remarkable solid carbohydrogen found in the quicksilver mines of Idria. Its composition is C_7H_7 , or perhaps $C_{21}H_7$; it colors oil of vitriol intensely blue, forming a coupled acid. Succisterene, a solid body obtained by Pelletier and Walter in the distillation of amber, has the same composition, and colors sulphuric acid blue. It is, therefore, in all probability, identical with idrialine.

Ozokerite, or fossil-wax, is found in large masses in the bituminous schist of Slamick, in Moldavia. When distilled, it yields a substance like wax, and also a good deal of paraffine. Ozokerite is very fusible, and burns with a bright flame.

Fichtelite is a fusible, volatile, crystallizable solid, found in branches of pine-trees, in the peat of the turbaries in the Fichtelgebirge. It appears to have the formula $C_{20}H_{12}$, and is probably derived from essence of turpentine, $C_{20}H_{12}$.

Tekoretine; phylloretine; xyloretine; and boloretine; are the names of four resinous compounds, found in the peat of Denmark, on the remains of pine-trees. Tekoretine and phylloretine are both fusible, volatile, and crystallizable. The former appears to be $C_{10}H_8$, the latter C_8H_8 . Xyloretine is less fusible, and is decomposed by heat. It crystallizes, and its formula is said to be $C_{20}H_{12}O_4$, which only differs from that of sylic acid by 1 eq. hydrogen. Boloretine is fusible, but does not crystallize. Its formula is $C_{20}H_{12} + 3H_2O$, but it occurs also with 5 and 6 eq. of water.

Asphaltum; mineral pitch; pitch of Judea. — These are the names of certain substances of similar characters, found in different parts of the world, as in Trinidad, in Hanover, and at the Dead Sea, in Palestine. They all resemble pitch in aspect, and are composed of a dark brown resin, mixed with more or less of

a brilliant black matter, asphaltene, $C_{20}H_{16}O_2$, or of a liquid volatile oil, petroleue, $C_{20}H_{14}$. The former of these is probably an oxide of the latter. The different kinds of asphaltum are much used for water-proof cements, and for pavements, or roofs. Naphtheine is a somewhat analogous substance, found in the limestones of the Maine et Loire.

Petroleum and naphtha. — In certain spots, in the neighborhood of the Caspian, in Ava, at the Tegernsee in Bavaria, at Amiano in Italy, and near Neufchatel, as well as in other places, pits dug in the earth become filled with water, on which floats, more or less abundantly, an oily matter, formerly called rock-oil. The purer kinds are little colored and very fluid, and when distilled with water, leave hardly any residue. These are called naphtha. Other kinds, as the petroleum of Rangoon in Ava, are dark-colored and semi-solid, but become liquid at 80° or 90° . These yield by distillation, first, much naphtha, nearly colorless, and then much paraffine, which is easily purified. Naphtha, when pure, has the Sp. G. 0.755, and its formula is C_8H_8 . Rectified naphtha is used for the purpose of preserving potassium and sodium, which have no action on it if water be not present. In many places the native naphtha is used to give light.

Reichenbach found that coal, distilled with water, yielded a little of an oil very similar to petroleum.

All the above substances are formed by the decay or destruction of organic matter, chiefly wood. It is not altogether improbable that those kinds which, like the *rangoon petroleum*, contain paraffine ready formed, may have been formed by the action of heat on beds of vegetable remains, situated pretty deep in the crust of the earth.

Soot and lamp-black are produced by the imperfect combustion of organic matters. They contain much carbon, mixed, in soot, with an acid resinous matter, and with a substance analogous to humus, but containing nitrogen, and called *absoline*. Lamp-black, besides a little resin and oily matter, often contains naphthaline, which may be extracted by alcohol.

SULPHURIZED AND NUTRITIOUS ANIMAL AND VEGETABLE PRINCIPLES. ALBUMINOUS SUBSTANCES.

We have already seen that some essential oils contain a large proportion of sulphur, and it is probable that these oils are derived from the decomposition of compounds existing in the plants which contain much sulphur, but the true nature of which is not yet known. But while such compounds only occur in a few plants, there is another class of sulphurized compounds which occur in all plants without exception. These compounds contain nitrogen and oxygen, both in considerable proportion to the carbon and hydrogen, and a small proportion of sulphur. They are all solid, and

when heated yield products containing ammonia and sulphur. They have neither a medicinal nor a poisonous action on the animal system, but are nutritious in the strict sense of the word.

Such are vegetable albumen, vegetable fibrine, and vegetable caseine, as well as animal albumen, animal fibrine, and animal caseine. The latter, when compared with the former respectively, are found to differ from them only in form, agreeing with them in all essential chemical characters. Every one of the six dissolves in strong hydrochloric acid, gently warmed, with a purple color; and all of them likewise dissolve in caustic potash, forming a solution which, according to Mulder, yields, after boiling, on the addition of acetic acid, a gelatinous precipitate containing no sulphur, while sulphuretted hydrogen gas is disengaged. Mulder named this precipitate *Proteine*, believing it to be the fundamental compound in the albuminous substances, in each of which it was combined with different small proportions of sulphur, phosphorus, and salts. The following table will explain his views, *proteine*, according to his analysis, being $C_{45}H_{31}N_5O_{12} = Pr$.

Crystalline humor contains	15 eq. <i>proteine</i>	+	1 eq. sulphur.	
Caseine	10 " "	+	1 " "	
Vegetable gelatine	10 " "	+	2 " "	
Albumen of eggs	10 " "	+	1 " "	+ 1 eq. phosphorus
Fibrine	10 " "	+	1 " "	+ 1 " "
Albumen of blood	10 " "	+	2 " "	+ 1 " "

In this table the salts are omitted.

Mulder's view, according to which the albuminous substances are all compounds of *proteine*, has been generally adopted, and is at first sight very attractive, as it not only accounts for the close agreement in composition and properties among the albuminous bodies, but also enables us to perceive how they may pass into each other.

But on a closer inspection, several things appear unfavorable to the theory of *proteine*. In the first place: in the above table, the albumen of eggs contains less sulphur than that of blood, whereas, in fact, it contains more. Secondly: in the table, albumen of eggs and fibrine have the same formula, yet their properties are totally distinct; while the *proteine* theory professes to explain difference of properties by difference of composition. Thirdly: recent analyses, according to the most accurate methods, have proved that those bodies contain three or four times as much sulphur as is assumed in Mulder's formulæ. Fourthly: it has been found impossible to obtain a *proteine* free from sulphur; for if the operation be continued as long as sulphur is found in the precipitate, the result is that at last no precipitate at all will be obtained. As long as acetic acid causes a precipitate, that precipitate contains sulphur. Fifthly: the presence of phosphorus in any other form than that of phosphates, in albuminous substances, has in no way been established,

and seems in the highest degree doubtful. Lastly: the best analyses we have render it very questionable whether, in reference to carbon, hydrogen, nitrogen, and oxygen, the albuminous bodies agree so closely as is supposed on the theory of Mulder.

Since, then, the existence of proteine has not been demonstrated, there appears no good reason for adopting the proteine theory; and we shall therefore describe the albuminous bodies without farther reference to it.

1. *Vegetable Albumen* has only been studied as yet in the coagulated or insoluble state. It occurs, however, dissolved, or in the soluble form, in vegetables, and especially in the oily seeds, along with caseine. It is always combined with alkali, to which it owes its solubility. Its distinguishing character is that of coagulating, or becoming insoluble when heated to from 140° to 160° . Once coagulated it no longer dissolves, even in the liquid in which it formerly quite dissolved. When a fresh vegetable juice is filtered and boiled, it yields a coagulum, which is nearly pure albumen. Its solutions are also coagulated by acids, by infusion of galls, by creosote, and by corrosive sublimate. When dried it is translucent. In all these characters it agrees with animal albumen. Its composition, so far as it has been ascertained, is the same as that of animal albumen; but the true formula, even of the latter, is unknown. We shall therefore state, under *Animal Albumen*, what is the result of the best analyses.

2. *Vegetable Fibrine* is the essential part of what is called the gluten of wheat. It is chiefly found in the seeds of the *cerealia*. When wheat, softened in water, is kneaded under water in linen bags, to obtain the starch, and the residuary masses are beat up with rods, the pure fibrine adheres in elastic, transparent filaments to the rods. These, after being treated by ether, to remove fat oil, are pure fibrine. When dried, it becomes grayish and translucent, like horn. When heated, it yields the usual products of animal matters; and when left to itself, in the moist state, it putrefies, disengaging fetid gases. It is quite insoluble in water. Diluted phosphoric and acetic acids dissolve it easily; these solutions are precipitated by ferrocyanide of potassium, and by infusion of galls. Diluted potash also dissolves it; and this solution, when neutralized by phosphoric or acetic acid, yields a precipitate which dissolves in an excess of either of these acids. (For the composition of fibrine, see *Animal Fibrine*.)

3. *Vegetable Caseine*. *Syn. Legumine*. — Is an essential part of the seeds of the *leguminosae*, and also of the oily seeds. It is only known in combination with acids and with alkalies. To obtain it, kidney-beans, lentils, or peas, are softened in water, then brayed in a mortar, the pulp mixed with much cold water, and strained through a fine sieve, which retains the husks and allows the caseine and starch to pass, the former dissolved, the latter suspended.

On standing, the starch settles to the bottom, leaving a solution of caseine which may be decanted. It is sometimes milky if much oil be present, sometimes clear. When exposed to the air, it quickly becomes acid, lactic acid being formed, and coagulates exactly as skimmed milk does when it becomes sour. The solution of caseine does not coagulate by heat, but, like milk, forms a pellicle which is renewed as fast as it is removed. It is coagulated by the addition of an acid, and the coagulum dissolves in an excess of all vegetable acids except acetic acid, which produces a permanent precipitate, as do the mineral acids. This precipitate is well washed with cold water, alcohol, and ether, dissolved in hot water with a little ammonia, and this solution is precipitated by alcohol. It still contains ammonia, but is otherwise nearly pure.

In this state it is like paste of starch, and when dried it is nearly transparent, and liquefies when heated. In water it softens and this paste is coagulated by acids, corrosive sublimate, infusion of galls, and creosote. Caseine is very soluble in tartaric and oxalic acids, also in caustic and carbonated alcalies if diluted. The coagula, or precipitates formed by mineral acids in solutions of caseine, are compounds of caseine with the acid: they are soluble in strong acids. For the composition of caseine, the reader is referred to *Animal Caseine*.

4. *Emulsine* or *Synaptase*, is the name given to a peculiar compound of this class, found in certain oily seeds, as in almonds, &c. An emulsion of these seeds is very like milk. On standing, the oil rises, like cream, to the top, and the watery liquid is now coagulated by acetic acid, as milk would be. It coagulates also by boiling; and in this case, the whey, separated from the coagulum, again coagulates on standing twenty-four hours, and is found to contain lactic acid. The emulsine agrees with albumen, in being coagulated by heat, and with caseine, in being coagulated by acetic acid. It exerts a peculiar decomposing agency on amygdaline, in which it is also itself decomposed.

Fungine is the substance of which mushrooms are chiefly composed. Its true nature is uncertain, but it contains nitrogen.

Gliadine is the name given to the viscid ingredient of gluten. It contains sulphur, and approaches in composition to vegetable albumen. It is probably a mixture.

When a vegetable juice, containing one or more of these compounds along with sugar, is exposed to the air, oxygen is absorbed, and a change is commenced in the albumen, fibrine, caseine, gluten, &c., which is soon communicated to the sugar, causing it to undergo the vinous fermentation. The temperature rises, and occasionally the viscous fermentation takes place, producing lactic acid, gum, and mannite. During fermentation, a gray deposit is formed; this is yeast or ferment. When the whole of the azotized

principles have not been decomposed or rendered insoluble, the liquid, if excluded from air, remains without farther change; but if air be admitted, the alcohol is converted into acetic acid, oxygen being absorbed by the azotized matters, the contact of which causes the alcohol also to absorb oxygen. When the sugar is in excess, only part of it is converted into alcohol, and part of the azotized matter takes the form of insoluble yeast, the rest being decomposed. The saccharine and spirituous liquid undergoes no farther alteration. All the above statements apply to the juice of the grape and to the formation of wines and vinegar.

When the juice, as that of the grape, contains tartaric acid, ethers are formed, which give the liquid a peculiar smell and flavor, such as œnanthic ether, which is characteristic of all wines. When a juice contains sugar and caseine, it is most apt to undergo the viscous fermentation, or, at least, the caseine favors the production of lactic acid from the sugar. But at a high temperature, such as 100°, butyric acid is formed, instead of lactic acid.

Vegetable fibrine, as it is found in wheat flour, is subject to continual alteration by contact with water; and in this state it has the singular property of converting starch into dextrine, a soluble gum, and then into sugar. This remarkable power is best seen in germinating grain, as in malt, of which a small part mixed with a large quantity of starch in a thick paste, and warmed to 150° or 160°, very soon renders the whole quite fluid and dissolved, and finally converts it into grape sugar. That part of the fibrine which acts on the starch has become soluble in water. It is called diastase.

Diastase is made by rubbing up malt with a little water, expressing the mixture, adding just enough alcohol to separate the albumen, and to allow the liquid to filter. The filtered liquid, mixed with more alcohol, deposits the diastase. It is purified by being repeatedly dissolved in water and precipitated by alcohol. It is finally dried at a temperature of 100° or 110°. Thus prepared, diastase cannot be a pure compound, but it possesses in a high degree the power of promoting the solution of starch, that is, its conversion into dextrine and sugar. One part of diastase can convert into dextrine, with a little sugar, no less than 2000 parts of starch. Diastase is evidently fibrine altered, and still more prone to change. Its solution cannot be kept; it becomes acid, and loses its action on starch.

Malt is made by softening barley in water, and then exposing it to the air in moderately thick layers, at a moderate temperature, turning it frequently. In about four days the seeds germinate, if they have not been allowed to become too hot, and if the air has had free access. As soon as the germ has acquired the length of the seed, the operation is checked by drying the seeds in a current of warm air. They now constitute malt. In this operation, much

carbonic acid is given off, oxygen being no doubt absorbed; the azotized matter in the seeds has undergone a change, and has acquired the properties of diastase; and the starch has in part disappeared, its place being supplied by grape sugar and dextrine.

When the malt is infused in warm water, the metamorphosis of the starch is completed, and the whole dextrine passes into sugar, which dissolves, along with extractive matter and salts. The solution is called must. When sufficiently concentrated, hops and yeast are added, and fermentation being carried on, the result is beer or ale, according to the strength of the must. When the malt has been in part roasted, the beer becomes very dark colored, as in the case of porter.

To obtain grain spirit, the meal, either of barley, oats, or rye, or a mixture, is digested in warm water along with 1 part of malt for 4 of meal, till the mass, at first thick, becomes fluid, a proof that all the starch has been metamorphosed. Yeast is then added, and, after fermentation, the must or wort as it is called, is distilled and rectified. Potato spirit is obtained in the same way, only using potato starch, instead of barley meal or rye flour.

Many other vegetable matters, and many fruits, may be made to yield spirit, malt or diastase being used in all cases where starch is to be converted into sugar.

Potato spirit is accompanied by the hydrated oxide of amyle, or oil of potato spirit: grain spirit by an oily matter, consisting chiefly of margaric and cœnanthic acids, probably in part as margaric and cœnanthic ether, and of a volatile oil, called by Mulder oleum siticum, that is, oil of grain. Wine spirit, that is, brandy, contains cœnanthic ether, and the spirit of molasses, or rum, owes its flavor to butyric ether. The oils which contaminate potato and grain spirit are offensive and even injurious to health: they are included by the Germans under the general term *Fuseloel*.

Panification. — Bread may be made from any flour containing, as all good flour does, vegetable fibrine, sugar, and starch. The flour being made into a paste with warm water, and yeast being added, it is set aside in a warm place. After a time, more flour is kneaded into the mass, which has begun to rise, and the whole is now heated in the oven, or baked. The yeast induces the vinous fermentation in the sugar of the flour, and the alcohol and carbonic acid escaping, raise the bread and render it porous. The starch in general is little changed, but the sugar disappears, as well as a part of the gluten or fibrine. To avoid this loss, bread is now raised by means of carbonate of soda or ammonia and a diluted acid, which are added to the dough, and the effect is perfectly satisfactory. Equally good or better bread is obtained, and the quantity of flour which will yield 1500 loaves by fermentation, furnishes 1600 by the new method, the sugar and fibrine being saved.

The addition of a little alum to the dough is useful in arresting that decomposition in the flour which is apt to occur if it have been kept in a moist place. Too much alum cannot be introduced, as it would prevent the fermentation.

The nutritive properties (using the word in its strict sense) of different kinds of flour or meal are directly proportional to the fibrine or albumen they contain; because it is these substances alone which can be converted into blood or flesh. Hence a working man requires more oat bread than wheat bread to restore the daily waste of the body, oatmeal containing rather less fibrine, &c. than wheat flour. The starch is consumed in the body, up to a certain point, but beyond this it is discharged in the excrements. We shall see hereafter what its function probably is. Even the best wheat flour contains more starch than is consumed; and the excess is greater in other grains.

In germination, the azotized principles of the seeds become soluble and prone to further change. When now dissolved, they are in the same state as those of the grape juice which at once cause fermentation when air is admitted. Diastase is merely gluten, that is, fibrine, in this soluble form or period of change.

When left in water, gluten swells, putrefies, and disengages carbonic acid, hydrogen, and sulphuretted hydrogen gases: it then becomes fluid and ropy, the water becomes very acid, and contains a peculiar compound called caseous oxide, with acetate, phosphate, and caseate of ammonia. When vegetable caseine putrefies, it gives out the odor of putrid cheese, and yields sulphuretted hydrogen gas.

Ferment, Yeast, Lees of Wine.—These are names given to the deposit formed in fermenting liquids, which possess the property of exciting fermentation in must, wort, grape juice, infusion of malt, or solution of sugar. When solution of sugar is employed in excess, the ferment gradually diminishes, till about 15 per cent. are left, of a substance containing no nitrogen, and insoluble. This is cellulose, or hordeine. On the other hand, in grape juice, or infusion of malt, the ferment is reproduced from the azotized principles present.

Mulder and Schlossberger have shown that ferment is composed of regular cells, formed of cellulose, and containing an azotized matter, very easily decomposed, which is an albuminous compound. This body rapidly decomposes the deutoxide and persulphide of hydrogen, but loses this property after it has been heated to 212° . Mulder thinks that, after boiling, it is a superoxide of proteine.

The power of yeast or ferment to act on sugar is destroyed by boiling water, by absolute alcohol, by pyroligneous acid, salts of mercury, essential oils, sulphurous acid, &c.

Caseous oxide, caseic acid, or aposepidine, are names given to the crystalline compound formed during the putrefaction of gluten

under water. It contains nitrogen, but its formula is unknown. It is soluble in water, insoluble in alcohol.

We now proceed to the consideration of the parallel compounds, animal albumen, fibrine, and caseine.

5. *Animal Albumen* is hardly known in a state of purity. The purest appears to be that prepared by exactly neutralizing serum of blood or white of egg with acetic acid, and adding a large quantity of water. The albumen separates in translucent flocculent masses, which, when washed with water, assume the aspect of paste.—(*Denis*). Albumen is best known in the form of the serum of the blood and that of white of egg.

Serum of blood, dried in a very gentle heat, leaves a translucent mass, which dissolves completely by digestion with water. Both in this form, and in the preceding, it dissolves far more easily in the most diluted alkaline solutions.

White of egg consists of very delicate cells, filled with a ropy liquid. By beating with water, the cells are broken, and are afterward deposited, being insoluble. Dried at a gentle heat, white of egg is yellow, translucent, and brittle. In water it again softens into its original state. When calcined, it leaves 6 or 7 per cent. of salts, common salt, carbonate, phosphate and sulphate of soda, and phosphate of lime.

The action of heat on albumen is remarkable. When heated alone, or after dilution with water, to between 145° and 165° , it coagulates into the well-known white elastic mass, which, when dried, becomes yellow, horny, and brittle. It is now quite insoluble in water; but if, after being coagulated and dried, it is placed in water, it swells up into the original elastic mass of coagulated albumen.

The albumen prepared by the process of Denis dissolves readily not only in acids and alkalies, but also in neutral salts, such as nitrate or sulphate of potash or soda. It is owing to the presence of such salts in serum and white of egg that their albumen is soluble in water. When the pure albumen of Denis is dissolved in solution of nitre, it is coagulated by boiling, exactly like serum.

Solutions of albumen are coagulated by acids; the addition of free alkalies prevents even the action of heat. Serum and white of egg, when mixed with water, being both alkaline, may be neutralized carefully by acids, without coagulation. Acid solutions of albumen are precipitated by corrosive sublimate and ferrocyanide of potassium, by infusion of galls, by creosote, and by alcohol. The real difference between soluble and insoluble or coagulated albumen is not yet known.

When albumen putrefies, it yields sulphide of ammonium, sulphuretted hydrogen, and other products. When heated, it burns with the odor of burnt horn or animal matter.

The composition of albumen is not yet ascertained with sufficient precision to enable us to deduce its formula from the analysis alone. The following table contains a few of the best analyses of the albumen of eggs:—

	Mulder.	Scheerer.	Rüling.	Verdeil.	
Carbon	54·086	55·000	51·91		
Hydrogen	7·100	7·073	7·15		
Nitrogen	15·650	15·920			
Oxygen	22·157				
Phosphorus	00·330	22·007			
Sulphur	00·667		1·717	2·164	2·054

A glance at these numbers is sufficient to show that the agreement is not such as to enable us to fix a formula, and more especially such a formula as that of Mulder, containing 10 eq. of proteine, that is, 400 eq. of carbon, 310 of hydrogen, 50 of nitrogen, and 120 of oxygen. A very trifling variation in the carbon, for example, makes a difference of 20, 30, or more atoms in the deduced formula, and the above analyses exhibit a variation of 3 per cent. in the carbon. Again, the sulphur in the analyses of Rüling and Verdeil amounts to more than 3 times the quantity obtained by Mulder, who admits one eq. of sulphur in egg-albumen. The presence of phosphorus, as admitted by Mulder, has not been proved; and lastly, the most recent analyses indicate from 16 to 17 per cent. of nitrogen.

It is clear, therefore, that we cannot hope to fix the formula of albumen by mere analysis, at least for the present; and the only method which promises better results, is the study of the products of its decomposition. In the case of gelatine and caseine, a beginning, as we shall see, has been made, and it is more than probable that albumen will yield similar results.

6. *Animal Fibrine* is found in blood, chyle, and lymph dissolved, and forms the chief part of the muscles. It may be obtained by whipping up blood with rods, when it adheres to the rods, and is finally purified by kneading with water to remove coloring matter, and by digestion with alcohol and ether, which dissolve fatty substances. When dry it is somewhat similar to albumen, and when heated burns with the same smell, leaving from 0·17 to 2·55 per cent. of ashes, phosphates of lime and magnesia. Recent fibrine loses, in vacuo, about 80 per cent. of water, the greater part of which it again takes up when placed in water. When long boiled with water, it slowly dissolves; and when left long, that is, for some months, under water, it gradually disappears.

The fibrine of venous blood dissolves, at a gentle heat, in solutions of acetate of soda, sal ammoniac, and nitre. These solutions are coagulated by heat, and exhibit the properties of dissolved albumen. Muscular fibrine may also be thus dissolved; but neither arterial fibrine, nor the fibrine of the buffy coat, can

undergo this change. Venous fibrine loses this property by exposure to the air, when it absorbs oxygen and gives off carbonic acid. Fresh fibrine rapidly decomposes deutoxide of hydrogen; but boiling water or alcohol deprive it of this property.

The most striking character of fibrine is its spontaneous coagulation, as in the blood; which is also seen in vegetable fibrine in some juices. In regard to acids and alcalies, fibrine acts like albumen.

The composition of fibrine approaches closely to that of albumen, and the best analyses do not admit of being reduced to a formula at present. We may hope for a better result when the products of its decomposition shall have been minutely studied.

7. *Animal Caseine* is chiefly found in milk. It is not known in a state of purity, but only combined with bases or acids, for both of which it has a powerful attraction. Uncombined caseine is insoluble: in milk it is dissolved by virtue of the potash which renders that fluid alkaline. If carefully neutralized by an acid, milk is not coagulated, but it is then coagulated by boiling. The coagulum or curd formed by excess of acids is very soluble in oxalic and tartaric acids, sparingly so in the mineral acids. This coagulum contains, along with caseine, a good deal of the acid employed.

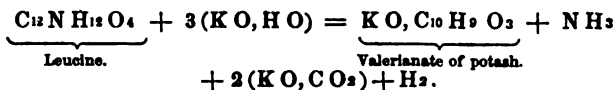
The coagulum caused in milk by alcohol, yields, when burned, 10 per cent of ashes, chiefly phosphate of lime. What is called soluble caseine is a compound containing much potash. With lime, baryta, &c., caseine forms insoluble compounds.

The composition of caseine is not accurately known, as the body known under that name contains 6.5 per cent. of ashes. But in regard to the other elements, it agrees pretty nearly with albumen and fibrine, the existing analyses exhibiting the same variations. It certainly contains less sulphur than albumen or fibrine; for while albumen contains from 1.7 to 2 per cent., and fibrine from 1.3 to 1.6 per cent., caseine appears to contain no more than from 0.85 to 1.0 per cent of sulphur.

As in the case of the two preceding compounds, so also in this, no formula can safely be deduced from the analyses. But the study of the products of decomposition of caseine, which has been commenced, promises to lead to better results.

Schlossberger has succeeded in resolving caseine into two nitrogenized bodies, one of which contains all the sulphur, the other none. Liebig has discovered that when caseine is melted with caustic potash till hydrogen gas begins to escape along with ammonia, the residue dissolved in water, and mixed with acetic acid, deposits a crystalline compound, tyrosine, $C_{16}H_{15}O_5$, which merits a detailed investigation. The mother liquid, when farther concentrated, yields leucine, a body already known as a product of the action of potash on gelatine. Its formula is $C_9H_{11}O_4$.

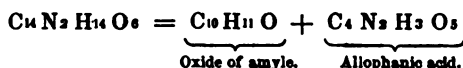
Moreover, if the original fused mass be supersaturated with tartaric acid, and distilled, it yields valerianic acid; and if the heat has been longer continued, butyric acid also is obtained. The origin of the valerianic acid is obviously the action of potash on leucine previously formed.



Leucine contains, excepting 1 eq. of hydrogen which is wanting, the elements of a compound of 1 eq. cyanic acid, 1 eq. oxide of amyle, and 2 eq. of water:



But when hydrated cyanic acid is made to act on hydrated oxide of amyle, it yields a compound which, although very similar to leucine, is yet quite distinct, being the allophanate of oxide of amyle, analogous to the allophanate of oxide of ethyle. Its formula is,



According to Bopp, caseine, when acted on by hydrochloric acid, yields products, among which are found, in large proportion, tyrosine and leucine. It has long been known that albuminous bodies yield leucine, when acted on by sulphuric acid. It appears, therefore, that these compounds have a tendency to yield definite and crystalline products, the study of which offers the best method of ascertaining their formulæ.

It has also been found that caseine, when oxidized by certain methods, yields the same varied products as gelatine. (*See Gelatine.*)

In the spontaneous decomposition of caseine we again meet with valerianic acid, along with butyric acid and the other volatile oily acids.

Milk, or any other solution of caseine, when evaporated in the air, forms a pellicle, which is renewed as fast as it is removed. This is insoluble, and yields ashes containing lime and phosphate of lime.

Milk may be analyzed by drying it up in vacuo, dissolving the butter by a mixture of ether and alcohol, and the sugar of milk and salts by cold water. The caseine remains in this way undissolved, the salts having been first removed.

When exposed to the air, milk undergoes a peculiar change. The caseine enters into decomposition, and this decomposition passes to the sugar of milk, which yields a little lactic acid, and this causes the caseine not yet decomposed to coagulate. But

the decomposition continues; the sugar of milk is at last entirely converted into lactic acid, mannite, and gum; and if the acid be neutralized, and fresh sugar added, it will undergo the same change as long as any caseine remains. This is the method followed for obtaining lactic and lactates. The coagulum separated from the whey when first formed, and pressed out, forms cheese. In making the better kinds of cheese, the milk, instead of being allowed to coagulate spontaneously, is coagulated by contact with water, in which part of the lining membrane of a stomach has been infused. This infusion is called rennet, and it acts by virtue of containing albumen or gelatine in a state of decomposition, which is at once communicated to the sugar.

When milk spontaneously coagulated, is exposed to a heat of from 75° to 85° , without any addition, the sugar of milk passes into grape sugar, and vinous fermentation ensues. The fermented milk, distilled, yields a spirit containing traces of butyric ether.

If sugar is made to ferment with caseine at about 100° , carbonic acid and hydrogen gases are disengaged, and butyric acid is formed in a large quantity.

The chief mineral substances in milk are potash and phosphate of lime, which are found in its ashes. The ashes also contain sulphates, although milk does not. The sulphuric acid in the ashes is derived from the oxidation of the sulphur of the caseine.

The proportions of water, caseine, sugar of milk, butter, and salts, are very variable in milk. It generally contains about 86 per cent of water, 4 to 7 of caseine, 3.5 to 5.5 of butter, and 3 to 5.5 of sugar of milk and salts. For the best method of analyzing milk, proposed by Haidlen, I must refer to the "*Annalen der Chemie und Pharmacie*," xlv., 274. By this method Haidlen obtained as follows:

	From Cow's Milk.	Human Milk.	Do.
Butter	3	3.4	1.3
Sugar of Milk, and salts soluble in alcohol	4.6	4.3	3.2
Caseine and insoluble salts	5.1	3.1	2.7
Water	87.3	89.2	92.8
	<hr/> 100.0	<hr/> 100.0	<hr/> 100.0

The colostrum, or milk given immediately after parturition, differs from normal milk in containing 15 to 25 per cent. of albumen, with less caseine, butter, and sugar of milk.

The milk of bitches, according to Simon, contains from 14.6 to 17.4 of caseine, 16.2 to 13.3 of butter, and no sugar.

Cheese is caseine in a state of incipient or progressive decomposition or putrefaction. In the finer kinds of cheese, there is a large proportion of butter, and to the volatile acids of the butter may be ascribed the flavor of cheese. Some kinds of cheese are full of what are called eyes, that is, hollows, caused by the

formation of bubbles of gas ; and in these hollows a liquid is sometimes found, containing free ammonia, a product of decomposition, which greatly heightens the flavor. When the blue mould appears in cheese, it is in a state of rapid decay or eremacausis, and much ammonia is given off. Little is yet known of the chemical differences in the making of different kinds of cheese. The richest are made almost entirely from cream, as Stilton and Parmesan. Others, as Gruyère, Gloucester, Cheshire, and Dutch cheese, are made with fresh uncreamed milk, or mixtures of this with cream ; and more or less salt is used, as well as different methods of coagulating, in different places.

Animal Mucus is somewhat analogous to albumen, when dry.. In water, it softens and swells, like tragacanth. It is precipitated by picric acid. It contains sulphur.

8. *Horny Matter*. — This name may be given to the substance of which the epidermis, hair, wool, silk, feathers, nails, claws, hoofs, horn, shell, and probably also sponge, are composed. All these substances dissolve in potash-lye when heated with it, giving off ammonia, and forming a solution from which, by neutralization with acetic acid, a white gelatinous matter is precipitated. (See *Proteine*.) They all contain sulphur. Sponge leaves $3\frac{1}{2}$ per cent. of ashes, among which is found iodide of potassium. All the above substances, when heated or burned, give out the same peculiar and well known smell, known as that of burnt feathers.

GELATIGENOUS TISSUES.

Under this head we place several tissues which yield to boiling water a substance which on cooling forms a jelly, or may be called gelatine. They are chiefly found in the cellular membrane, the skin, the membranes in general, the tendons, ligaments, bones, cartilages, &c.

The cellular tissue and the membranes are chiefly formed of gelatinous matter, which is insoluble in cold water and acids. It combines with salts, as corrosive sublimate, persulphate of iron and alum, forming insoluble compounds which do not putrefy, as gelatine itself so readily does.

The gelatine of the skin, when moist, combines with tannic acid, if steeped in a solution of that acid, and is converted into leather. While the true skin is gelatinous, the epidermis is more allied to horn.

Chondrine is the name given to the gelatine of the cartilages.

Gelatine or glue is that given to the gelatine of the bones and hoofs, skins, &c. of animals. Isinglass is made from the air-bladder of fishes, and is nearly pure gelatine.

1 part of pure gelatine, dissolved in 100 of hot water, forms a jelly on cooling. A solution of isinglass is completely precipitated by infusion of nut-galls.

Chondrine and gelatine, in solution, are distinguished by acids, alum, and salts of lead, which precipitate chondrine but not gelatine. In regard to other tests, they agree. ~~That~~ of either may be detected by tannic acid.

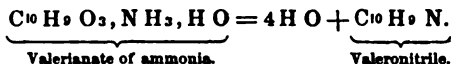
By the action of chlorine on gelatine, there is formed what is called chlorite of gelatine, consisting, according to Mulder, of chlorous acid and gelatine.

By the action of potash, gelatine is converted into sugar of gelatine, or glycoll, a substance already described as an artificial base, or into a mixture of sugar of gelatine and leucine.

The composition of gelatine is not more accurately known than that of the albuminous substances already mentioned. It approaches to them in composition, but, so far as we know, it cannot pass into albumen, fibrine, or caseine, as these bodies can pass into each other, and even into gelatine. Hence it is not fitted for the formation of blood, and cannot be called strictly nutritious.

When gelatine is oxidized by means of bichromate of potash and sulphuric acid, it yields, according to Schlieper, the following products: 1. hydrocyanic acid; 2. acetic acid; 3. valerianic acid; 4. benzoic acid; 5. a new oil, valeronitrile; 6. another new oil, valeracetoneitrile; and 7. a heavy oil, with an odor of cinnamon, not fully studied. Marchand obtained also hyduret of benzoyl.

Valeronitrile, $C_{10}H_9N$, corresponds to benzonitrile, a compound recently discovered among the products of the action of heat on benzoate of ammonia; and may be derived from valerianate of ammonia, as follows:



When acted on by alkalies, it takes up water, and is again converted into valerianic acid and ammonia.

Valeracetoneitrile, $C_{28}H_{24}N_2O_6$, contains the elements in 2 eq. of 4 eq. valeronitrile, and 3 eq. hydrated acetic acid. It is resolved by alkalies, water being taken up, into ammonia, which escapes, and acetic and valerianic acids.

It is obvious that the full investigation of the products of decomposition of gelatine will ultimately lead us to its true formula.

Bone. — The gelatine and other animal matters in healthy bone constitute from 37.5 to 44 per cent.; the rest is earthy matter. In rickets and mollities ossium, the cartilaginous matter amounts to from 63 or 70 to 80 per cent., and the phosphate of lime is diminished in proportion, not exceeding, in some cases, 12 or 13 per cent.

The proportions of gelatine and earthy matter vary in different animal species.

The earthy ingredients of bone are, phosphate of lime, carbonate of lime, fluoride of calcium, phosphate of magnesia, with small quantities of common salt, soda, &c.

Bone or ivory-black, obtained by calcining bones in retorts, contains all the earthy and saline matters, with a large proportion of charcoal intimately mixed with them. It probably contains nitrogen. Qu ? as paracyanogen or mellone ?

THE BILE.

This animal fluid, collected from the liver in the gall-bladder, is slightly alkaline, and has a viscid, oily consistence. It has, when fresh, a golden-yellow color with a tinge of green, and becomes darker when exposed to the air. Its taste is bitter and persistent, with a sweetish after-taste. It is perfectly miscible with water, and its aqueous solution froths like solution of soap.

When dried in the vapor bath, bile leaves a yellow mass, which dissolves in alcohol, leaving undissolved a little mucus. The alcoholic solution is deep green, but may be decolorized either by animal charcoal, or by the cautious addition of baryta, which forms an insoluble compound with the coloring matter. The decolorized alcoholic solution of bile still contains cholesterine, which is separated by adding ether, till the solution becomes slightly turbid: on standing, pure bile is deposited in crystals, the formula of which is $\text{NaO} + \text{C}_{44}\text{H}_{86}\text{NSO}_2$. — (*Verdeil*.)

The solution of bile is precipitated by neutral acetate of lead, but the liquid becomes acid. If the free acid be neutralized, acetate of lead produces a fresh precipitate, the liquid again becoming acid. Tribasic subacetate of lead precipitates at once the whole of the organic matter of the bile, but an excess of the precipitant is apt to redissolve a part of the precipitate, which is also soluble in alcohol. Mineral acids cause a resinoid precipitate in solution of bile.

Bile in solution may be recognized by the property of striking a purple color with solution of sugar and sulphuric acid.

Purified bile, when calcined, leaves a white ash, composed chiefly of carbonate of soda, with traces of phosphate of soda and common salt. The ash amounts to 12 per cent., of which upward of 11 consist of carbonate of soda.

It is, therefore, evident that bile is composed of soda united to an organic compound, having the characters of an acid, although a feeble one, and in some respects analogous to the fatty and resinous acids. This compound, which is the whole organic or combustible part of the bile, is called choleic or bilic acid, and bile is the choleate of soda.

Choleic acid is best prepared by making an alcoholic solution of 8 parts of pure bile, and dissolving, with the aid of heat, in this, 1 part of effloresced (monohydrated) oxalic acid. The oxalate of soda separates in crystals. The filtered liquid, diluted with a little water, is digested with carbonate of lead, till all oxalic acid is removed. Any lead that may be dissolved is separated by sulphur-

etted hydrogen, and the filtered solution evaporated in the water heat. Choleic acid may also be obtained by the action of dry hydrochloric acid gas on a solution of pure bile in absolute alcohol, and by several other processes, of which one may be noticed. Pure bile is precipitated by subacetate of lead, and the precipitate brought with water to the boiling point. Sulphuric acid is now added, drop by drop, until the precipitate has lost its peculiar consistence. The liquid is then filtered, and any dissolved lead separated by sulphuretted hydrogen.

To purify choleic acid it is dissolved in a very small quantity of alcohol, and precipitated by ether, which retains in solution fatty matters. The probable formula of choleic acid is $C_{44}H_{86}NSO_{10}$, $HO = C_{44}H_{84}NSO_{10}$.

When dried in the water-bath, or in vacuo, over sulphuric acid, choleic acid, if prepared from decolorized bile, is colorless, or nearly so, and has the aspect of gum. It is resinous and friable when dry, but its powder attracts moisture strongly, and becomes agglomerated together. Its solution is distinctly acid to test paper. The addition of mineral acids causes a separation of choleic acid in oily drops, which are soluble in pure water.

Pure choleic acid, when heated on platinum foil, burns with flame, leaving a voluminous coal which finally burns away without residue of ashes. When choleic acid leaves an alkaline ash, it is because it contains undecomposed bile, choleate of soda; in fact, it may be called acid choleate of soda, a substance which has been described as a distinct ingredient of the bile by several chemists.

Numerous analyses of pure bile (deducting the ashes) and all choleic acid, both prepared in many different ways, by different chemists, as Demarcay, Theyer and Schlosser, Kemp, Enderlin, Verdeil, and others, agree so well together, that no doubt can be entertained in regard to this point, that the bilic or choleic acid of ox bile is a substance of uniform composition, and that the acid in bile has the same composition as that which is obtained in the separate state by the processes above given.

Farther, if the choleate of lead, purified from phosphate, chloride, &c., of lead, by solution in alcohol, be acted on by carbonate of soda, choleate of soda (artificial) is obtained; and this salt, when pure, is found to differ in no one respect from pure bile, or natural choleate of soda, and is, therefore, regenerated bile. Its composition is the same as that of bile.

Choleate of soda has already been described as purified bile.

Acid choleate of soda has been at different times known as biliary matter, and as bilifellic acid with excess of biline. — (*Berzelius*.) But the biline of this chemist, and also his sugar of bile, are nothing more nor less than either pure bile or choleic acid. Platner has lately obtained the acid choleate of soda crystallized.

which is a strong additional argument in favor of the opinion that the bile is a uniform and definite compound of choleic acid, and that all the numerous compounds described by Berzelius and others as constituents of bile, are products of the decomposition of choleic acid. This is a consideration of the utmost importance, with reference to the production of bile in the animal body, to its functions, and in short to chemical physiology.

Choleate of lead (basic). — This salt, precipitated by subacetate of lead, has the characters of a plaster, as choleate of soda has those of a soap.

PRODUCTS OF THE DECOMPOSITION OF BILE.

The recent discovery of 38.6 per cent. of sulphur in taurine, and of nearly 4 per cent. in choleic acid, renders it impossible to give at present a satisfactory account of the various metamorphoses of the bile, until the researches, rendered necessary by these discoveries, shall be concluded. In the meantime, the only compounds the formulæ of which are known with any degree of certainty, are choleic acid and taurine. The formula of choleic acid must be considered doubtful, till we know what becomes of the sulphur of the bile in its formation.

1. *Choloidic acid*. — This acid is formed by the action of hydrochloric acid, when boiled with bile. It differs from choleic acid in containing no nitrogen. Its formula is $C_{80}H_{120}O_{11}$. Its production is attended with the formation of taurine. Choloidic acid is resinous or rather pitchy in aspect, softened by the heat of boiling water, insoluble in water and ether, soluble in alcohol. Probable formula $C_{80}H_{120}O_{11} = C_{80}H_{118}O_{10}, H_2O$; but as that formula was ascertained before the presence of sulphur in choleic acid was known, it must be considered doubtful.

By the action of nitric acid, choloidic acid is converted into a variety of products, among which are: 1. Several of the oily acids of the series $(CH)_n + O_2$; 2. a heavy pungent volatile oil, which by the action of potash yields nitrocholic acid, $C_{24}H_{38}N_4O_9$, H_2O , and cholacrole, another pungent oil, $C_{24}H_{38}N_2O_{13}$; 3. choloidanic acid, $C_{16}H_{22}O_6$, H_2O ; and 4. cholesteric acid, $C_{24}H_{38}O_4$, H_2O , so called because it is also formed by the action of nitric acid on cholesteroline.

2. *Taurine*, $C_4H_7N_2O_6$. — This substance is found in the liquid which has deposited the choloidic acid. When pure, it forms large prisms, neutral, with a cooling taste, soluble in water, and very permanent, not being decomposed by strong nitric acid.

3. *Cholic Acid*. — This is another non-azotized acid, formed when bile is acted on by fusion with caustic alkalies, which disengage the nitrogen as ammonia. It resembles the fatty acids, or rather the resinous acids. It forms large transparent tetrahedra, soluble in alcohol and ether, nearly insoluble in water. Formula, $C_{24}H_{38}O_6$, H_2O ?

4. *Dyslysine*. — This is the name given by Berzelius to a compound formed during the action of hydrochloric acid on bile. It is very sparingly soluble in hot alcohol. (Hence its name, from *δυσ*, and *λυσις*, solution). It has a resinous aspect, and the formula $C_{60}H_{88}O_7$, that is, choloidic acid minus 4 eq. water.

The fellic acid and cholinic acid of Berzelius are mixtures of some of the above, or of other products, with unaltered choleic acid. They do not exist ready formed in bile, according to Theyer and Schlosser.

5. *Cholic acid*, (Gmelin). — This is an acid, containing nitrogen, formed when choleate of lead is acted on by acetic acid. It forms fine needles of a sweet and pungent taste, very soluble in alcohol and in hot water. Its formula is unknown.

6. *Cholanin acid* is a resinoid acid, found in putrid bile, and very similar to choloidic acid, if not identical with it.

7. *Fellanic acid* accompanies the preceding. It forms transparent prisms, and may possibly be cholinic acid. At all events, it is not established as a distinct compound; but is a product, probably a mixed one, of some of the changes of so complex a substance as choleic acid.

The coloring matter of the bile when dry is reddish-brown, but dissolves in potash with a yellow color, becoming greenish-brown in the air. Its solution, mixed with excess of nitric acid, becomes first green, then blue, violet, red, and finally yellow. The same changes of color are seen in serum, chyle, or urine charged with bile, as in jaundice.

BILIARY CONCRETIONS.

The calculi or concretions found in the gall-bladder are generally composed of cholesterine, with more or less coloring matter. Sometimes the cholesterine is so pure that alcohol dissolves it entirely and becomes hardly colored; at other times coloring matter alone is found. The former case occurs in the human subject; the latter generally in the ox.

Lithofellic acid is an acid found constituting the mass of certain concretions called *bezoar orientale*, and said to be found in the stomach of certain antelopes; but which are, no doubt, biliary concretions.

Lithofellic acid is fusible, gives off when heated a fragrant vapor, and has when cut or rubbed in the concretion the lustre of wax. It dissolves in hot alcohol, and forms brilliant six-sided prisms, insoluble in water. Formula, $C_{28}H_{38}O_8$ — (*Elling and Will*); $C_{28}H_{38}O_7$, H O — (*Wöhler*).

Nitric acid converts it into a new acid containing nitrogen. Formula, $C_{28}H_{38}NO_{11}$.

When distilled, lithofellic acid loses 2 eq. water, and yields pyrolithofellic acid, $C_{28}H_{34}O_6$.

BRAIN AND NERVOUS MATTER.

This substance consists of water to the extent of about 80 per cent. ; of albuminous matter, 7 per cent. ; and of several peculiar fats, among which are cholesterine, and another beautifully crystalline fat, resembling cholesterine but distinct from it.

Cerebric acid. — This is a fatty acid, peculiar to the nervous matter. It is purified by means of ether, which removes an oily matter, and by crystallization in hot alcohol. It forms white granular crystals, slightly soluble in water, especially when hot, although the greater part is not dissolved, but swells up into a gelatinous paste. It melts when heated, and when burned leaves a very acid coal. It contains both nitrogen and phosphorus, which distinguishes it from the ordinary fat acids. Its salts are very soluble in alcohol, as well as in water.

Oleophosphoric acid. — This acid is dissolved, in combination with soda, by the ether used in purifying cerebric acid ; but it is hardly known in a state of purity, being mixed with a neutral oil, cerebroleine, with cholesterine, and with cerebric acid, in small quantity. With alcalies it forms soaps, exactly similar to the salts dissolved from brain by ether. When boiled with water or alcohol, it is resolved into cerebroleine and phosphoric acid. Of the latter it yields about 2 per cent.

Cerebroleine is purified by cold alcohol, which dissolves the oil, leaving undissolved all the cholesterine and cerebric acid. Its composition is the same as that of the oleine of human fat.

The cholesterine of the brain appears to be identical with that of bile. The brain also contains traces of oleic and margarinic acids. When it putrefies, the oleophosphoric acid disappears entirely.

The most important point in the chemical history of the brain is that it contains both fat and albumen, the two extremes of the animal products, and substances (cerebric and oleophosphoric acids) of a composition intermediate between that of albumen and that of fat. These bodies, however, appear to contain even a larger proportion of phosphorus than albumen. It is not yet known where the cerebric and oleophosphoric acids are produced : whether in or by a special organ, as the bile is by the liver ; or whether in the circulation generally. It will be seen hereafter that the blood does contain traces of cholesterine and other fatty matters ; and, indeed, as the blood also contains bile, it may be supposed that the liver does not form the bile, but merely separates it from the blood, it having been previously formed. In like manner, even if there should be found an organ connected with the formation or secretion of nervous matter, still the function of that organ might be only to separate cerebric acid, previously formed, from the blood. At all events, we cannot doubt that the very remarkable composition of the acids of the brain has an important relation to the functions of that organ, and that the production of

those acids forms an essential part of the vital process going on in the body.

Liebig has lately observed that the brain contains no kreatine, (a body found in urine and in the juice of flesh), but that when triturated with barytic water, two acids are taken up by that base, forming salts, one of which is insoluble, the other soluble, in alcohol. Both dissolve in water, and the solution in both cases yields a white precipitate with acids. The acids in question are therefore insoluble in water, and probably allied to fat acids, but they have not yet been examined.

Dr. R. D. Thompson has also been for some time engaged in the study of the brain, and his researches are anxiously looked for.

GASTRIC JUICE.

This juice, as extracted from the stomach of executed criminals, is colorless or slightly yellow, turbid, and distinctly acid. It contains free acids along with chlorides of potassium and sodium.

The nature of the free acid present in the gastric juice has been disputed. When it is distilled, free hydrochloric acid is obtained, and this is often, perhaps always, accompanied by butyric acid; but it must be remembered that these acids are volatile, and that therefore their presence in the distilled liquid affords no proof of their existence in the free state in the gastric juice. On the other hand, Lehmann obtained from the gastric juice, by a peculiar process, a salt of magnesia, which he analyzed, and which Liebig has shown to be lactate of magnesia. There can be no doubt of the presence of phosphoric acid, free or combined; and it is most probable that in the normal juice, the fixed acids, phosphoric and lactic, are, in part at least, free, while the volatile acids, hydrochloric and butyric, are present in the form of salts. In the distillation, the latter are expelled in the free state, the fixed acids taking their place. This view is confirmed by the phenomena exhibited by the juice of flesh, (See Liebig's *Researches on the Chemistry of Food*, and the next section of this work), which undoubtedly contains free lactic and phosphoric acids, (or what is the same thing, acid phosphates and acid lactates), along with chlorides, and appears to have a very close resemblance to the gastric juice.

The property of dissolving or digesting food, such as albumen, fibrine, caseine, &c., is owing in part to the presence of free acid, and in part to the presence of part of the lining membrane of the stomach dissolved, and in a state of change. The gastric juice converts into chyme, or digests, albumen, fibrine, &c., out of the body as well as in it, if the temperature of the stomach be kept up; and water acidulated with a trace of hydrochloric acid, and afterward left for 24 hours in contact with the lining membrane of a stomach, acquires in a very high degree the solvent power of the

gastric juice. Water thus prepared dissolves in 8 to 12 hours, at the temperature of from 86° to 104°, hard-boiled white of egg, &c., which requires 4 days at a temperature of 158° to 176° to be dissolved by water merely acidulated with the same proportion of acid, but not placed in contact with the stomach. This latter fluid, however, dissolves meat better than it does albumen, because the meat supplies some membranous matter in a state of change, by which the solution of the fibrine is finally promoted.

All attempts to isolate the supposed principle—pepsine as it was called, which is supposed by some to be the solvent of food in the stomach—have failed. The gastric juice has only yielded traces of animal matter, and we have not yet any proof that its solvent action depends on a peculiar compound, and is not rather the effect of a kind of fermentation induced in the food by contact with the particles of dissolved epithelium, themselves in a state of change, and consequently of motion. On the whole, then, taking into account the facts of artificial digestion, it appears most probable that digestion is a process analogous to fermentation in the conditions under which it takes place, namely, a certain temperature, and contact with azotized matter in a state of decomposition; but differing from the usual forms of fermentation in its phenomena, no gas being disengaged, and its chief result being the solution of an originally insoluble matter.

JUICE OF FLESH.

The muscular mass of animal bodies is chiefly composed of muscular fibre (fibrine), colored by blood, contained in innumerable small vessels, of those vessels, of nerves, of tendinous matter, and of cellular tissue. More than $\frac{3}{4}$ of its weight are water, which, holding in solution a great variety of substances, penetrates every part of the mass, and constitutes the *juice of flesh*, as it is termed. This fluid is contained either in peculiar minute vessels or in the cells of the cellular tissue, and when the flesh is finely chopped and pressed, the juice is obtained, more or less mixed with blood. The best method is to mix the chopped flesh with water, to squeeze out the mass, and to repeat this process if necessary. In this way, the juice of flesh is obtained in a somewhat diluted state, and, as already stated, not free from blood.

This fluid has recently been studied by Liebig (Researches on the Chemistry of Food*) with very interesting results. It is uniformly and strongly acid, and the acids present are lactic acid in large quantity, phosphoric acid, a new azotized acid, inosinic acid, and in smaller quantity some other organic acids, not yet examined. No sulphuric acid is present, save a trace from the

* London : Taylor & Walton. 1847.

blood. The bases are potash in large proportion, both as phosphate, lactate, inosinate, &c., and as chloride of potassium; soda in much smaller quantity, chiefly as chloride of sodium, (and probably derived from the blood, at least for the most part); magnesia; lime; the latter in much smaller proportion; and kreatinine. The juice contains, besides, albumen dissolved, which is coagulated by heat and amounts to from 2 to 3 per cent. of the weight of flesh. The insoluble residue of fibrine, &c., amounts when dry to 17 or 18 per cent., so that the average composition of flesh will be nearly as follows:

	Water	78
	Fibrine, vessels, nerves, cells, &c.	17
Soluble matter	{ Albumen	2.5
	{ Acids and bases, organic and inorganic, chlorides, and kreatine	2.5
		<hr/> 100.0

It is obvious, that in order to study with success the soluble matters not coagulated by heat, we must operate on large quantities of flesh, since, for example, 10 lbs. of flesh will not yield more than 4 oz. of these substances, among which are five or six acids, and as many bases, besides chlorides and kreatine. Thus, from 10 lbs. of beef, only about 50 grains of kreatine can be obtained.

Kreatine — This substance was first noticed by Chevreuil in the soup or extract of meat, but as he obtained it in very small quantity, and other chemists did not succeed in procuring it, its composition was unknown, and its existence was even doubted, as an ingredient of flesh, Berzelius having suggested that it might be an accidental product of decomposition. Liebig showed that it is always present in all kinds of flesh, at least in all those tried by him, namely, in the flesh of the horse, ox, ox-heart, sheep, pig, calf, roe-deer, hare, marten, red-deer, fox, fowl, and pike. Schlossberger had shortly before obtained a trace of it from the flesh of an alligator, although too little for analysis, and I have since found it in the flesh of pigeon, skate, cod and haddock. Liebig observed that when the juice containing it is evaporated, the kreatine is destroyed or rendered uncrystallizable by the free acid. By neutralizing, therefore, the juice obtained as above mentioned, (after heating it so as to coagulate the albumen, and separating the coagulated albumen by filtration), with baryta water, and evaporating to the consistence of syrup at 130° or 140°, he obtained the kreatine in quantity amply sufficient to allow him to study its composition and characters. The following table contains his results and my own in regard to the preparation of kreatine obtained from several kinds of flesh. It will be seen that in all it is small, varying from 0.607 to 3.21 per 1000.

					Liebig.	Gregory.
1000 parts of the flesh of fowl yielded of kreatine					3.20	{ 3.21 2.90
"	"	ox-heart	"	"	..	{ 1.375 1.418
"	"	cod	"	"		{ 0.935 1.710
"	"	pigeon	"	"	..	0.825
"	"	horse	"	"	0.72	..
"	"	ox	"	"	0.697	..
"	"	skate	"	"	..	0.607
"	"	haddock	"	"	..	1.504

Fowl yields the largest proportion, but kreatine is obtained much more cheaply from cod. I find that the chopped cod, well mixed with little more than its weight of water, and pressed out, yields a fluid, which, when neutralized (after the coagulation of the albumen) by baryta, filtered, to separate the phosphate of baryta, and gently evaporated, till, on cooling, it forms a thin jelly, deposits, on standing, kreatine, in large crystals, nearly pure. In one experiment, 25 lbs. of cod yielded 164 grains; in another, 30 lbs. yielded 356 grains. The crystals, by one recrystallization from 6 or 7 parts of boiling water, are rendered quite pure. The kreatine obtained from haddock was less pure than that from skate or cod, and was evidently mixed with a less soluble matter, the nature of which I have not had time as yet to ascertain.

Kreatine forms brilliant hard prismatic crystals, efflorescing at 212° , very soluble in hot water, less so in cold water, sparingly soluble in alcohol. It is neutral, and its formula is $C_5 N_3 H_{11} O_6 = C_5 N_3 H_9 O_4 + 2 H O$. By the action of acids, kreatine is resolved into the new base, kreatinine and water; and by that of bases, into the new base sarcosine, and urea, as already explained.

Kreatine has been discovered, along with kreatinine, in urine. Pettenkofer obtained, by the addition of chloride of zinc to a concentrated extract of urine, a crystalline precipitate, containing chloride of zinc and an organic matter, the composition of which he found to be $C_5 N_3 H_9 O_4$. Liebig has proved that this substance is resolved, by the action of alcohol, into kreatine, $C_5 N_3 H_{11} O_6$, and kreatinine, $C_5 N_3 H_7 O_4$, and that it was, in fact, as analyzed by Pettenkofer, a mixture of those substances, in the proportion of 3 eq. of the latter to 1 of the former. The original crystals of Pettenkofer were a mixture of free kreatine, with a compound of chloride of zinc with kreatinine.

The addition of chloride of zinc to the mother liquid which has deposited the kreatine from the juice of flesh, yields the compound of Pettenkofer, so that kreatinine exists ready formed in the juice of flesh.

Lactic Acid. — This acid, as an ingredient of the juice of flesh, is very interesting; and it is remarkable that Liebig, who demon-

strated its absence in normal urine, (in which, according to Cap and Heury, it exists in combination with urea,) should have been the person who detected it in flesh. It is present in large quantity, and occurs as abundantly in the flesh of carnivorous as in that of herbivorous animals. Its origin and formation in the former is not yet explained, and is a problem of much interest.

The presence of lactic acid in the juice of flesh is also important, as readily accounting for its presence in the gastric juice, which, as we have seen, is also acid. The lactic acid in the juice of flesh is obviously consumed in respiration, as will be explained hereafter.

Inosinic Acid. — This acid has been little studied. Its formula is $C_{10}N_2H_8O_{10}, H_2O$, and it forms, with baryta, a salt which crystallizes in silvery scales.

Phosphoric Acid. — This acid exists in large proportion in the juice of flesh, in the form of acid tribasic phosphate of potash, $PO_5 \left\{ \begin{array}{l} KO \\ 2HO \end{array} \right\}$, a salt which is always produced when phosphoric acid is made to act on chloride of potassium or salts of potash. This salt is strongly acid, and chiefly contributes to the acidity of the juice.

It is most important and worthy of remark, that the blood which is separated from the juice of flesh only by the finest membranes, cell walls, or parietes of vessels, is invariably alkaline, containing the common phosphate of soda, $PO_5 \left\{ \begin{array}{l} 2NaO \\ HO \end{array} \right\}$, a salt which is always formed when phosphoric acid acts on chloride of sodium or salts of soda, and which is strongly alkaline.

Here we observe, first, that while soda is essential to blood, potash is equally essential to the juice of flesh; secondly, that in these two fluids, soda and potash cannot, as in so many other cases they can, replace each other; thirdly, that by this arrangement, an acid and an alkaline fluid are constantly in close vicinity to each other, separated only by membrane, at all parts of the body; fourthly, that being at the same time in contact with muscle and nerve, the conditions of electric currents are present; while such currents, as is known, have recently been proved by Matteucci to exist. Lastly, that animals cannot form blood, unless their food contain, along with phosphates, salts of soda, or at least chloride of sodium, so that when they are fed on the land plants of certain soils, in which sodium is nearly absent, common salt must be given to them.

The function of the phosphate of magnesia, which occurs in large quantity in the juice of flesh, is not yet even conjectured; but it cannot be doubted that all the substances present, organic as well as inorganic, have each a special part to perform.

SALIVA.

The chief use of the saliva is to assist in digestion, whether by itself containing animal matter in a state of change, or by its remarkable power of inclosing and retaining bubbles of air, the oxygen of which commences the change necessary to digestion, on coming in contact with the food or the stomach and gastric juice. To serve this purpose, the saliva has a very great degree of viscosity, so that it froths up easily, and the froth does not fall readily. It is alkaline, and contains hardly more than 1 or 2 per cent. of solid matter, partly mucus, partly the usual salts, partly a peculiar soluble matter, ptyaline. The salts of the saliva are the chlorides of potassium, sodium, and calcium, some potash, and soda, with a large proportion of bone earth. It appears also to contain a trace of sulphocyanide of potassium: at least it reddens with persalts of iron; and although acetates do this, there is some reason to ascribe the effect here to sulphocyanides.

The *pancreatic juice* resembles saliva, but appears to be slightly acid, and contains 8 or 9 per cent. of solid matter, including ptyaline and a matter like caseine. This juice is added to the chyme in its passage through the duodenum, along with the bile and intestinal mucus.

EXCREMENTS.

Urine. — The chyme, after receiving the pancreatic juice, the bile, and mucus, passes along the intestine, where the absorbents or lacteals take up the fluid part, leaving the insoluble portions. The chyle or absorbed fluid is partly conveyed into the abdominal veins, and partly made to pass through numerous glands (in which process it loses its acid reaction, becoming alkaline), from which it proceeds to the thoracic duct, and is then, with the lymph, poured into the vena cava to mix with the venous blood.

In the meantime, the insoluble parts of the chyme are rejected, and accumulate in the large intestines, various gases being disengaged, such as carbonic acid, hydrogen, carburetted hydrogen, nitrogen, and sulphuretted hydrogen.

The solid excrements of man contain very little matter soluble in water, and consist of woody fibre, with fatty, resinous, and waxy substances, and finally the insoluble salts of the food, namely, phosphates of lime and magnesia, with traces of soluble salts, and some silica.

The urine of man contains urea and uric acid, also hippuric acid, kreatine and kreatinine, and other organic compounds very imperfectly known. Its acid reaction, according to Liebig, depends on the fact that phosphate of soda dissolves uric and hippuric acids, forming an acid solution. If 40 grains of dry phosphate of soda

$\text{P O}_5 \left\{ \begin{array}{l} 2 \text{ Na O} \\ \text{H O} \end{array} \right\}$ 15 grains of uric acid, and 15 grains of hippuric

acid, be dissolved in 1 lb. of hot water, a solution is formed which on cooling deposits $7\frac{1}{2}$ grains of uric acid, and the remaining liquid forms an artificial urine, which, like the natural, is acid. It contains also phosphoric acid, magnesia, often ammonia, soda, phosphate of soda, common salt, sulphuric acid, or sulphate of soda, in short, the soluble salts of the food, along with sulphuric acid formed by the oxidation of the sulphur of the tissues. The addition of ammonia to urine causes a precipitate of phosphate of lime.

Fresh urine, filtered (to separate mucus) into a perfectly clean vessel, keeps unchanged for weeks or even months; but if in contact with decomposing animal matter, the urea is speedily transformed, by putrefaction, into carbonate of ammonia, while phosphate of lime is precipitated, the urine becoming strongly alkaline.

The urine of the herbivora contains much uric acid, also hippuric acid; that of the carnivora contains more urea, and is strongly acid: uric acid predominates very greatly in the urine of birds, and that of reptiles is nearly pure acid urate of ammonia.

When benzoic acid is administered internally, it appears in the urine as hippuric acid, which latter acid is generally present in small quantity in urine. The acid reaction of human urine is not owing to lactic acid, as was formerly supposed, but to free uric acid dissolved by the phosphate of soda. The urine is sometimes neutral, and always becomes alkaline, when the food contains salts of potash or soda with organic acids, because, the acids being oxidized in the body, yield carbonates of the alkalies. It is evident, therefore, that by attention to diet, the urine may be brought into any desired condition.

When water, or a very weak saline solution, is taken into the stomach in large quantities, it is rapidly absorbed by endosmosis, and the urine becomes more and more diluted, till at last it resembles the water that has been taken. But if a solution containing as much saline matter as the blood, or a little more, is taken into the stomach, it is not absorbed, and the stomach becomes so loaded that the experiment cannot be continued. If, again, the solution be much stronger, the water of the blood passes outward by exosmosis, and produces diarrhoea. This explains the purgative action of neutral salts, which is well exemplified by sprinkling salt on a portion of fresh membrane such as bladder, or on meat, both of which yield water and are soon swimming in brine.

The salts of the urine and of the excrements, being derived directly from the food, vary according to its nature, the soluble inorganic salts of the food being found in the urine, the insoluble salts in the excrements. Thus the ashes of the food of the carnivora contain no carbonates, but are rich in phosphates, and such also is the case with the salts (or ashes) of their excreta, liquid or solid. In fact, if we know the nature and composition of the ashes

of the food, we can tell at once the salts of the urine. In an adult animal, the quantity of salts excreted is precisely equal to that contained in the ingesta, and, therefore, by altering the food, we can alter at pleasure the nature of the salts in the urine.

As an example, we may here adduce the case of the horse, which animal consumes, in his food, a certain quantity of mineral substances, derived ultimately from the soil:

THE HORSE

Consumes of Mineral Substances.		Excretes of Mineral Substances.	
	oz.		oz.
In 15 lbs. of hay,	18.61	In the urine	3.51
In 4.54 lbs. of oats,	2.46	In the fæces	18.36
In water,	0.42		
21.49		21.87	

The above result is one obtained by actual and very careful experiment, and the nature of the salts is found to be the same, as indeed must obviously be the case, as long as the animal does not change its weight. A growing animal will retain the phosphates in part to aid in forming bone, and an old or wasting animal will give out more salts than are taken in.

It is obvious that analyses of urine or excrement are unnecessary, if we can examine the food; and that in general, they must be useless, since we can never expect the same result twice, unless where the food is not varied.

The excrements, according to Liebig, represent the incombustible and unburned, or partially burned ingredients of the food, and if we view the body as a furnace in which the animal heat is produced by the oxidation or combustion of the food, they correspond to the soot and ashes of a common fire. That they contain partially oxidized matter is proved by the fact, recently observed by Liebig, that the albuminous compounds, when partially oxidized by fusion with potash, yield, on the subsequent addition of an acid, volatile matters, possessing, according to the albuminous substance employed, the peculiar odors which characterize the fæces.

Guano, so highly prized as a manure, is the decayed excrement of sea-fowls, which was originally, like that of reptiles, and indeed also of birds in general, mixed urine and fæces, the urine being solid or semi-solid, and consisting of urate of ammonia. It varies much in the proportions of its ingredients, both because the original excrement must have varied according to the food of the birds in different places, and also because some specimens have not been so long exposed to air and moisture as others, and some are almost fresh. Thus some guano contains upward of 30 per cent. of uric acid, while in other specimens hardly a trace of that acid is left. The better qualities of guano contain much ammonia, partly free, or as carbonate, as proved by its odor, partly combined, as sal

ammoniac, oxalate, urate, and phosphate of ammonia and magnesia. They also contain phosphate of soda and much phosphate of lime, the latter being derived from the bones of the fish on which the birds fed. There are also found sulphate of potash and soda, and oxalate of lime, in guano. The remainder is water, and a brown matter like humus.

It is easy to see that guano must act chiefly as a source of ammonia and earthy and alkaline phosphates, so valuable to growing plants, especially to those cultivated for food, and that its value depends very much on the amount of phosphates it contains. But while the value of guano is unquestionable, let us not overlook the fact, that while we are ransacking the most remote islands for guano, that substance supplies us with nothing but the mineral salts and the ammonia which have formed crops of vegetables and races of animals at some former period, and that it differs in no essential point from the fresh or modern excreta of man and animals nearer home, which excreta, at least those of man, the most valuable of all, we allow to be carried into the sea in quantities which may be measured by the food we consume. In fact we take out of the sea, in the shape of guano, only part of what we throw into it in the contents of our common sewers. These valuable matters, instead of being carefully collected and preserved, as in China, are sent to form the food of sea-plants: on these plants animals feed, which animals serve as food to fish. The fish are consumed by sea-fowl, and we recover in their excrement a part of what we are throwing away. Another part of what we lose we recover in this country, at a great expense, in the shape of bone earth, which, however, must be taken from other countries. We shall return to this subject: meanwhile, let us express a hope that Europe will at length follow generally, as in some districts it has done, the rational example set by the eminently practical Chinese, of restoring to the soil, as nearly as possible, in the shape of excreta, what we take from it in our crops and cattle, and thus keeping up its fertility.

URINARY CALCULI.

These are of various kinds, according to the peculiar condition of the urine.

Uric acid calculus is the most frequent, being the usual deposit when the urine is acid. Its origin as a calculus, or deposit, that is, in abnormal quantity, is owing to deficient aeration, much oxygen being required to resolve it into soluble compounds, such as urea, carbonate of ammonia, or even oxalic acid. Hence sedentary habits, highly carbonized food, and indulgence in strong wine, all favor its production; the first by diminishing the supply of oxygen, the two latter causes by seizing on the oxygen to the exclusion of the uric acid. It is easily recognized by the action of potash,

which dissolves it, and forms a solution from which acids precipitate uric acid; or by nitric acid, which dissolves it with effervescence, and yields, on evaporation of the solution, a deep red stain, becoming purple with potash. Uric acid calculus is commonly tinged more or less red or brown. When pure it is entirely dissipated before the blowpipe.

Urate of ammonia also occurs, and is distinguished from uric acid by disengaging ammonia when dissolved in potash.

Phosphate of lime is very frequent when the urine is neutral or alkaline. It is white and earthy, soluble in nitric acid, and precipitated by ammonia. It is fixed in the fire.

Phosphate of ammonia and magnesia is also pretty frequent. It dissolves easily in acetic acid, and when heated gives off ammonia, leaving a solid mass, soluble in acids.

Fusible calculus is a mixture of the two preceding. It melts readily before the blowpipe.

Oxalate of lime constitutes the mulberry calculus, and often appears as minute crystals in the urine. When heated, it leaves carbonate of lime; or if heated in a tube with oil of vitriol, it gives off carbonic oxide. It dissolves in acids, and is precipitated by alkalies.

Carbonate of lime occasionally, but very rarely, constitutes a urinary calculus, easily recognized by the action of hydrochloric acid, which dissolves it with effervescence, and by a red heat, which leaves quicklime.

Cystic oxide or cystine, and xanthic oxide, are very rare calculi. Their characters and composition have been given under *Uric Acid*.

LYMPH.

This fluid may be looked on as blood devoid of its coloring matter. When drawn from the vessels, it coagulates like blood, from the separation of fibrine; and the liquid in which the coagulum has formed itself, coagulates, when heated, like the serum of the blood. Human lymph contains about 96 per cent. of water, and variable proportions of albumen, fibrine, and salts, the salts amounting to nearly 2 per cent.

BLOOD.

This important fluid, from which the whole animal body is formed, and by which it is supplied and nourished, is a thick, somewhat viscid, alkaline liquid, of a slight saline taste, and a peculiar faint odor. It is deep red and opaque, and has a density of 1.0527 to 1.057.

It is made up of an immense number of *globules* or flattened disks, floating in a limpid yellowish fluid. When drawn, it soon coagulates, forming a trembling jelly, which gradually contracts,

expressing a yellowish liquid, the *serum*, which is occasionally turbid, and is always alkaline to test paper, and saline to the taste.

The coagulation consists in the separation of the fibrine previously dissolved, which, owing to some unknown cause, assumes the insoluble state, forming a fine network or jelly, in which the globules are inclosed. If the blood be beaten with a rod, the fibrine separates perfectly and adheres to the rod; but it is in the form of white filaments, and the globules remain suspended in the serum, no jelly whatever being formed in this case. Or if the fresh blood be mixed with 8 times its bulk of solution of sulphate of soda, no coagulum is formed, the fibrine remains dissolved, and a sediment is deposited which contains the globules unaltered.

The *red globules* thus prepared may be collected in a filter. Pure water added to them, or to the coagulum of blood, rapidly alters their form, and in fact dissolves them into an opaque liquid. This action of water is thus explained: the globules are formed of a thin, colorless, and transparent coat, inclosing a very soluble coloring matter. They float in a saline liquid, in which there is equilibrium between the contents of the globules and the fluid surrounding them. But when the latter is diluted with water, the equilibrium is disturbed, and endosmosis takes place, by which the contents of the globules acquire so greatly increased a volume, that the globules burst and their contents are dissolved in the water. The torn membranes of the globules may be detected by the microscope.

In saline solutions, the globules do not absorb water any more than in the serum. When collected in a filter, the globules form a red mass of the consistence of honey, consisting of fibrine and albumen, the latter in combination with the coloring matter. In a concentrated solution of chloride of calcium, the globules lose water by exosmosis, and contract in volume. If now placed in pure water, the globules again swell, and burst, forming a jelly which dissolves in water. The solution, on standing, deposits fibrine in white membranous masses, and the supernatant liquid, when boiled, is coagulated, indicating the presence of albumen.

The *coloring matter* of the blood is contained in the globules in combination with albumen, but is unknown in a state of purity. The compound of albumen and coloring matter is of a deep red color, becoming bright in contact with air or oxygen, and being rendered nearly black by carbonic and sulphurous acids, sulphuretted hydrogen and sulphides. Protoxide of nitrogen gives it a purple color.

The red compound gives 2 per cent. of ashes, of which $\frac{1}{2}$ is peroxide of iron; and iron is uniformly present in red blood, which is the only animal product in which it occurs. This iron cannot be detected in the globules or their contents by the usual tests, but

after passing chlorine through the red solution till the color is destroyed, the iron may be detected by ferrocyanide of potassium.

When the red compound of albumen and coloring matter above mentioned is moistened with oil of vitriol, so gradually as not to become warm, a pasty mass is obtained, which attracts moisture from the air and forms a red jelly. If this be very gradually rubbed up with pure water, it contracts into a dark red matter, which is surrounded with a colorless or yellowish liquid. This liquid is found to contain all the iron, and the dark matter, when calcined, leaves a white ash entirely free from iron, if the operation has been well performed. I have repeated this interesting experiment, first devised, I believe, by Sanson, which proves that, although the red compound contains iron, yet the color does not necessarily depend on that metal; for the color is altogether uninjured by the complete removal of the iron just described, although the coloring matter actually obtained in this experiment is not the original coloring matter of the blood, but modified.

The *hematosine* of Lecanu is also a product of decomposition. It is prepared by means of diluted sulphuric acid, alcohol, and ammonia, by a tedious process. It is dark brown, and forms red solutions with the alkalies, being insoluble in water, alcohol, and ether. It contains part of the iron of the blood, but as some kinds of hematosine contain $\frac{1}{4}$ or $\frac{1}{3}$ more iron than others, while its properties continue the same, it is obvious that the iron does not contribute essentially to those properties, such as the color. Hematosine contains 6 to 8 per cent. of iron.

But the iron serves an important purpose in the blood; and we have reason to think that it is present in the form of oxide, for sulphuretted hydrogen and soluble sulphides cause the blood to become first green and then black, owing to the formation of sulphide of iron—a character indicating either the oxide or some corresponding compound, and not a compound like ferrocyanogen, in which the sulphides cannot detect the iron. Moreover, we see that oil of vitriol dissolves out oxide of iron; and although alkalies and ferrocyanide of potassium do not detect it, this is owing to the blood being an alkaline liquid, and to the presence of so much animal matter.

It is from the blood that are formed the tissues, the cells, muscular fibre, nervous matter, &c., &c.; and we may, therefore, expect to find some relation between their composition and that of the blood. In fact, flesh, or muscular fibre, as it exists in the body, including vessels, nerves, fat, &c., has exactly the same composition as the blood has on an average of venous and arterial, or a mixture of both. We may, therefore, look on muscular fibre, or animal flesh, as simply blood more highly organized.

In addition to the substances mentioned above, namely, albumen, fibrine, coloring matter, and salts, blood also contains fat,

apparently cholesterine, along with fatty acids and a peculiar fat, called *seroline*.

The normal proportions of serum and clot are 87 per cent. of serum to 13 of clot. 1000 parts of human blood contain 869·15 of serum, of which 790·37 are water, 67·8 albumen, and 10·98 are salts and fatty matter: along with 130·85 of clot, containing 125·63 albumen and fibrine of the globules, and 2·27 hematosine, (a little fatty matter and traces of salts being present in all three), also 2·95 of fibrine, separate from the globules.

Venous blood contains more water and fewer globules than arterial blood.

The blood contains gases, chiefly carbonic acid and nitrogen, which it gives off in vacuo, or in a current of hydrogen. It is said to contain free oxygen, but this seems very improbable, when we reflect that fibrine absorbs oxygen, transforming it into carbonic acid, and that blood is instantly altered by contact with oxygen. The change from venous to arterial blood, from dark to florid, depends on the presence of oxygen, but also requires the presence of a saline solution. Indeed, a similar change of color takes place in vacuo if the clot of venous blood be there covered with a pretty strong solution of various salts.

One chief function of the blood is, after conveying oxygen to all parts of the system, to carry to the lungs, there to be exhaled, the carbonic acid formed in the extreme vessels. For this purpose it is admirably adapted, from the fact that it is alkaline, and that its alkalinity depends on the phosphate of soda, $\text{P O}_5 \left\{ \begin{array}{l} 2 \text{ Na O} \\ \text{H O}, \end{array} \right\}$ a salt, the solution of which absorbs carbonic acid better than a solution of carbonate, and, when in contact with air or oxygen, gives off *the whole of it*, whereas a carbonate, if it absorbed as much, would give up only half of the quantity absorbed. This important property of phosphate of soda has recently been demonstrated by Liebig; and we can now see why potash cannot replace soda in the blood, since the tendency of potash is to form an acid phosphate, $\text{P O}_5 \left\{ \begin{array}{l} \text{K O} \\ 2 \text{ H O}. \end{array} \right\}$ Liebig and Enderlin have also proved that the blood does not, as had been asserted, contain carbonate of soda.

THE NUTRITION OF PLANTS AND ANIMALS.

The animal and vegetable kingdoms of nature are connected together in a beautiful system of mutual dependence, exhibiting a perpetual circulation of certain elements through both, the mineral kingdom being the point of departure and that also where the circulation terminates, to recommence unceasingly.

Plants derive their nourishment exclusively from the mineral world. It is clear that the first plants must have done so; and

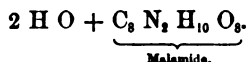
although the decaying remains of former plants now contribute to vegetation, we shall see that they do so under mineral forms, and not essentially; they promote vegetation, but are not indispensable to it.

The mineral food of plants, then, consists of carbonic acid, water, and ammonia, all of which are obtained from the atmosphere, and of sulphur (sulphuric acid,) phosphorus (phosphoric acid,) alkalies, earths, salts, and metals, all derived from the soil. Without the aid of the matters derived from the soil, the most abundant supply of carbonic acid, water, and ammonia, is of no use. But if a soil contain these necessary substances, plants will thrive in it, even if they have no carbonic acid nor ammonia furnished in the shape of manure beyond the usual atmospheric supply, *provided time be given*.

During germination—a process which goes on best in the dark—oxygen is absorbed, and carbonic acid given out. Heat is also generated. It cannot be doubted that a very essential part is performed also by *endosmosis*, that is, the tendency of water or of weak saline solutions to pass through a membrane or cell-wall, on the other side of which is a strong saline or saccharine solution. By this means, the first supply of water penetrates the cell-walls of the seed and its embryo, and there forms a strong solution; for the presence of moisture and oxygen induces putrefaction of a portion of the albuminous matter always present in the cells; this putrescent matter becomes a ferment, and converts the insoluble starch, stored up in the cells, into soluble sugar, as happens in an infusion of malt. But it likewise renders soluble the whole remaining albuminous matter, as happens when fibrine is left under water. Thus the cells become filled with a strong solution of sugar, albumen (fibrine or caseine) and salts, and now endosmosis rapidly goes on. The cells become distended, and those of the embryo are developed according to the vital law impressed on them at their formation, producing leaves by a constant formation of new cells. Such is the result of germination; but it must be noticed that already certain new compounds appear, apparently formed in the cells out of the carbonic acid, water, and ammonia supplied from the atmosphere either directly to the first leaves, or indirectly, through the water percolating the soil, to the cells of the radical fibrils, along with phosphates, alkalies, and common salt.

Here first comes into play that amazing chemical force, by which, in the vegetable cell, carbonic acid is decomposed, and its oxygen given out; while water, ammonia, and the mineral salts are all rendered available. This demands the aid of light, but, as already mentioned, even in germination, and in plants which are etiolated or grown in the dark, certain new compounds have been formed, such as occur under the influence of light also. Whether these are formed in the same way without as with light, is not known with certainty, but as in the dark oxygen is absorbed, not given out, we

may suppose that they are produced in germination by a process of putrefaction or destruction of more complex molecules, such as those of albumen. The substances here alluded to are certain vegetable acids, found in the juices of germinating seeds and etiolated plants, and especially malic acid and malamide or asparagine, formed from malate of ammonia by the loss of water. This body is very abundant in etiolated plants, such as asparagus and vetches grown in the dark; it is also found naturally in *Althæa officinalis*. Now we may suppose malic acid to be formed by the decomposition of albumen, along with ammonia, by a kind of fermentation, so long as light is absent; or it may be formed from the sugar by oxidation, a process active in germination. Thus 2 eqs. of dry grape-sugar, $C_{24} H_{34} O_{24}$, with 12 eqs. of oxygen, may yield 3 eqs. of hydrated malic acid, $3 (C_8 H_8 O_{10}) = C_{24} H_{24} O_{30}$, and 6 eqs. of water. The malic acid thus formed, in contact with ammonia, derived from the atmosphere or from albumen, will yield malamide (asparagine). $C_8 H_8 O_8, 2 N H_4 O =$



As soon as light, however, comes into play, the true vegetative process begins: carbonic acid is decomposed and oxygen given out, and the carbon of the carbonic acid, with varying proportions of oxygen and hydrogen from water, of nitrogen from ammonia, and of sulphur from sulphuric acid, produces with the aid of phosphates, alcalies, and salts, in the vegetable cell, all the vast variety of vegetable products. It is here that the prodigious chemical power of the vegetable cell comes into play, and this is so great, that it is able to perform, gradually, at the ordinary temperature, what the most powerful agencies of heat and electricity cannot do in the laboratory, namely, to decompose carbonic acid, *setting free its oxygen*. But we are not to suppose that the carbonic acid is totally decomposed into carbon and oxygen, and that the carbon, thus set free, combines with hydrogen, oxygen, nitrogen, &c., to yield vegetable products, for the insolubility of carbon would prevent this. Of a number of associated molecules of carbonic acid, some lose part of their oxygen, and the residue of these, with the remaining carbonic acid and water, &c., enters, at the moment of separation, into new forms of combination. It is, therefore, necessary to consider the effect of vegetation as it is manifested, first, on carbonic acid and water together; secondly, on these, with the addition of ammonia; and lastly, on all these, with the aid of sulphuric acid. The first yields the non-nitrogenous compounds; the second, the nitrogenised compounds; and the third, those which contain both nitrogen and sulphur.

Even when carbonic acid and water are brought together in the cell, this is not enough. There must be present, first, albuminous

matter, without which no active cell can exist; secondly, mineral matter, especially alkalies, phosphates, and salts. All these conditions being fulfilled, and light being admitted, we may suppose the first organic acid formed to be oxalic acid, the least complex of all. Crystallised oxalic acid is $C_2 H_2 O_4 = C_2 O_2, 2 H O + 4 aq.$ Now this is evidently formed from 4 eqs. of carbonic acid, $C_2 O_2$, and 6 eqs. of water, $6 H O$, together $C_2 H_2 O_{14}$, by the separation of 2 eqs. of oxygen. And this, which is performed with ease in the vegetable cell, we cannot do in the laboratory, although we can produce oxalic acid from more complex organic products, such as sugar, starch, and many others. It is found abundantly in plants of the genera *Rumex*, *Rheum*, *Oxalis*, *Sedum*, *Sempervivum*, in many lichens and others. The reader will observe that in the crystallised acid, 4 eqs. of water are merely water of crystallisation, and that the driest oxalic acid is only $C_2 H_2 O_4$ or $C_2 O_2, 2 HO$, the 2 eqs. of water being basic. Of course we may leave out 4 eqs. of water of crystallisation, and suppose dry oxalic acid to be derived from 4 eqs. of carbonic acid and 2 of water, $= C_2 H_2 O_{10}$, by the separation of 2 eqs. of oxygen as before.

Let us now ascend a step higher in the organic scale; to the formation, namely, of malic acid, which is more complex than oxalic acid. Now this acid may be formed, either from oxalic acid itself, or like oxalic acid, from carbonic acid and water, but in both cases by the separation of oxygen. In the former case, 2 eqs. of crystallised oxalic acid, $2 (C_2 H_2 O_4) = C_4 H_4 O_8$, by losing 6 eqs. of water and 8 eqs. of oxygen, yield $C_4 H_4 O_{10} = C_4 H_4 O_8, 2 H O$, or hydrated malic acid, which is bibasic. Or again, 2 eqs. of dry oxalic acid, $2 (C_2 H_2 O_2) = C_4 H_4 O_4$, taking up 2 eqs. of water, and losing 8 eqs. of oxygen, yield $C_4 H_4 O_{10}$, or hydrated malic acid. In the latter case, 8 eqs. of carbonic acid and 6 of water, together $C_4 H_4 O_{22}$, losing 12 of oxygen, yield $C_4 H_4 O_{10}$, or hydrated malic acid.

Tartaric and citric acids are easily shown to be producible in the same way. 2 eqs. of dry oxalic acid and 2 of water, together $C_4 H_4 O_6$, losing 6 of oxygen, yield $C_4 H_4 O_{12} = C_4 H_4 O_{10}, 2 H O$, hydrated tartaric acid. Or, 8 eqs. of carbonic acid and 6 of water, together $C_4 H_4 O_{22}$, losing 10 of oxygen, give $C_4 H_4 O_{12}$, hydrated tartaric acid. Again, 3 eqs. of dry oxalic acid and 2 of water, together $C_{12} H_6 O_{20}$, losing 12 of oxygen, yield $C_{12} H_6 O_{14} = C_{12} H_6 O_{11}, 3 H O$, or hydrated citric acid, which is tribasic. Or 12 eqs. $C O_2$, plus 8 $H O$, together $C_{12} H_8 O_{28}$, losing 18 of oxygen, give $C_{12} H_8 O_{14}$, or hydrated citric acid.

In like manner, every vegetable acid, and every one of the neutral compounds of carbon, hydrogen, and oxygen, may be derived, first, from some less complex acid or neutral compound, containing more hydrogen than itself; secondly, from a certain proportion of carbonic acid, to be determined by the number of eqs. of carbon in the com-

pound, and of water; oxygen, in all cases, being given off. As the proportion of oxygen to carbon and hydrogen diminishes, the acids become weaker, till the oxygen exactly suffices to form water with the hydrogen, when we have either very feeble acids, or neutral bodies, such as sugar, gum, and starch. As the oxygen is still further diminished, we have neutral, bitter, and acrid compounds, or colored bodies, or such as yield coloring matters, with ammonia and oxygen: further on still, we have aromatic oils and volatile quasi-resinous crystallisable acids; then resins; and lastly, when all the oxygen is expelled, certain oils, which are carbohydrogena. The following tabular view will furnish a comparative statement of the amount of carbonic acid and water required, and of oxygen given off, on the supposition that each compound is formed directly from carbonic acid and water. But, as we have seen, each may also be formed from any of those below it in the scale, that is more highly oxidised, as citric acid from oxalic acid, or sugar from citric acid. To illustrate this, if to citric acid, $C_{12} H_8 O_{14}$, we add 6 eqs. of water, we have $C_{12} H_{14} O_{10}$, and this, losing 6 eqs. of oxygen, yields $C_{12} H_{14} O_{14}$, or crystallised glucose. In like manner, 3 eqs. of malic acid and 16 of water, losing 18 of oxygen, yield the same sugar; or 3 eqs. of tartaric acid, with 10 of water, losing 18 of oxygen, likewise yield grape-sugar. These are changes which occur every day in ripening fruits, and it is probable that sugar, starch, and other compounds are really formed in the plant, not directly from carbonic acid and water, as in the table, but from some intermediate compound, as sugar is here shown to be from the three acids just mentioned.

Acid employed.	Water added.	Oxygen separated.	Glucose.
Citric $C_{12} H_8 O_{14}$	+ 6 H O	O_6	= $C_{12} H_{14} O_{14}$
Malic $3(C_4 H_4 O_6)$	+ 16 H O	O_{18}	= 2 ($C_{12} H_{14} O_{14}$)
Tartaric $3(C_4 H_4 O_8)$	+ 10 H O	O_{18}	= 2 ($C_{12} H_{14} O_{14}$)

But as these are merely intermediate steps in the whole process of deoxidation, by which sugar, starch, fat, oils, &c., are formed from carbonic acid and water, and the final result is the same whether these bodies be formed directly or indirectly, we shall confine ourselves, in the tabular view, to their direct formation from carbonic acid and water.

TABULAR VIEW OF THE PRODUCTION OF VEGETABLE COMPOUNDS FROM CARBONIC ACID AND WATER, BY DEOXIDATION.

GROUP I.—*Stronger Vegetable Acids soluble in Water.*

Substance formed.		Carbonic acid used. in eqs.	Water used. in eqs.	Oxygen separated. in eqs.
Name.	Formula.			
Oxalic acid, dry	$C_2 H_2 O_4$	4	2	2
Gallic acid	$C_7 H_2 O_8$	7	8	12
Tartaric acid	$C_4 H_4 O_8$	8	6	10

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Malic acid	$C_4 H_6 O_{10}$	8	6	12
Aconitic acid	$C_{12} H_8 O_{12}$	12	6	18
Citric acid	$C_{12} H_8 O_{14}$	12	8	18
Meconic acid	$C_{14} H_4 O_{14}$	14	4	18
Tannic acid	$C_{24} H_{22} O_{34}$	54	22	96
Kinic acid	$C_{28} H_{22} O_{32}$	28	22	56

The above are all acids, and in all but kinic acid the oxygen exceeds the hydrogen. Kinic acid is but a feeble acid. All other vegetable acids of similar properties to the above belong to this group, but those here given are sufficient to characterise it.

GROUP II.—*Indifferent Neutral Compounds.*

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Cellulose	$C_{12} H_{10} O_{10}$	12	10	24
Starch	$C_{12} H_{10} O_{10}$	12	10	24
Cane-sugar	$C_{12} H_{22} O_{11}$	12	11	24
Gum	$C_{12} H_{11} O_{11}$	12	11	24
Grape-sugar, dry	$C_{12} H_{12} O_{12}$	12	12	24
Do. crystals	$C_{12} H_{14} O_{14}$	12	14	24

This important group contains, in every instance, hydrogen and oxygen in the proportion to form water, so that the whole of the oxygen of the carbonic acid, but not that of the water, has been separated. They may be viewed, theoretically, as formed of carbon, *plus* water; thus starch may be $C_{12} + 10 H O$.

GROUP III.—*Neutral Bodies, chiefly Bitter, Acrid, Colored, or yielding Colors with Ammonia.*

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Mannite	$C_{12} H_{14} O_{12}$	12	14	26
Ordine	$C_{14} H_8 O_4$	14	8	32
Smilacine	$C_{18} H_{18} O_6$	18	15	45
Meconine	$C_{20} H_{10} O_8$	20	10	42
Quassine	$C_{20} H_{12} O_8$	20	12	46
Peucedanine	$C_{24} H_{12} O_8$	24	12	54
Salicine	$C_{28} H_{18} O_{14}$	26	18	56
Antiarine	$C_{28} H_{20} O_{10}$	28	20	66
Pectine	$C_{28} H_{21} O_{24}$	28	21	58
Hæmatoxyline	$C_{32} H_{14} O_{12}$	32	14	66
Popoline	$C_{40} H_{22} O_{16}$	40	22	86
Phloridzine	$C_{42} H_{24} O_{20}$	42	24	88
Limouine	$C_{42} H_{26} O_{18}$	42	25	96
Hellenine	$C_{42} H_{28} O_8$	42	28	106
Onleine	$C_{52} H_{34} O_{16}$	52	34	120
Elaterine	$C_{60} H_{28} O_{10}$	60	25	127

In this group, which is a very numerous one, various kinds of compounds appear. Mannite closely approaches to sugar; antiarine and elaterine are acrid poisons; salicine, phloridzine, popu-

line, and quassine, pure bitters; pectine, a gelatinising substance; hæmatoxyline, a colored body; orcine, forms a fine color with ammonia; and others are indifferent. It has lately been shown that populine, from poplar bark, is related to salicine, from willow bark. It is salicine, in which 1 eq. of hydrogen is replaced by 1 eq. of benzoyle, $C_{14} H_4 O_2$. This is proved by the fact that it may be made to yield salicine and compounds of the benzoic series. The fact is most interesting, as showing that the law of substitution prevails among very complex compounds, and explaining how similar compounds may be formed. The above are only examples. In the whole, not only the oxygen of the carbonic acid, but also part of that of the water, has been separated, so that the hydrogen remaining exceeds the oxygen.

GROUP IV.—*Oxygenated Volatile Oils, and Aromatic Acids related to them.*

Substance formed		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Oil of bitter almonds.....	$C_{14} H_8 O_2$	14	6	32
Benzoic acid.....	$C_{14} H_4 O_4$	14	6	30
Oil of spiræa.....	$C_{14} H_8 O_4$	14	6	30
Salicylic acid.....	$C_{14} H_6 O_4$	14	6	28
Oil of anise.....	$C_{16} H_8 O_4$	16	8	36
Anisic acid.....	$C_{16} H_6 O_4$	16	8	34
Cumarine.....	$C_{18} H_4 O_4$	18	4	36
Cumaric acid.....	$C_{18} H_4 O_6$	18	4	34
Oil of cinnamon.....	$C_{18} H_8 O_2$	18	8	42
Cinnamic acid.....	$C_{18} H_6 O_4$	18	8	40
Oil of cumine.....	$C_{20} H_{12} O_2$	20	12	50
Cuminic acid.....	$C_{20} H_{12} O_4$	20	12	48

In this group the oxygen is still further diminished. All the compounds are volatile, and the acids approach to resins in composition. The oils are fragrant, and yield the acids by simple oxidation; in fact, most of these oils are aldehydes.

GROUP V.—*Volatile Oily and Fatty Acids, of the Formula $(C_n H_{2n})_2 O_2$.*

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Formic acid.....	$C_2 H_2 O_4$	2	2	2
Oxide of methyle.....	$C_2 H_2 O$	2	3	6
Acetic acid.....	$C_4 H_4 O_4$	4	4	8
Oxide of ethyle.....	$C_4 H_6 O$	4	5	12
Glycerine, dry.....	$C_6 H_4 O_2$	6	4	14
Propylic acid.....	$C_6 H_6 O_4$	6	6	14
Butyric acid.....	$C_8 H_8 O_4$	8	8	20
Valerianic acid.....	$C_{10} H_{10} O_4$	10	10	26
Oxide of amyle.....	$C_{10} H_{12} O$	10	11	30
Caproic acid.....	$C_{12} H_{12} O_4$	12	12	32
Enanthylic acid.....	$C_{14} H_{14} O_4$	14	14	38
Caprylic acid.....	$C_{16} H_{16} O_4$	16	16	44
Pelargonic acid.....	$C_{18} H_{18} O_4$	18	18	50
Eutic acid.....	$C_{20} H_{20} O_4$	20	20	56

TABULAR VIEW OF RESINS AND CAMPHORS.

853

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Margaritic acid.....	$C_{23}H_{43}O_4$	22	22	62
Laurostearic acid.....	$C_{24}H_{44}O_4$	24	24	68
Cocinic acid.....	$C_{26}H_{46}O_4$	26	26	74
Myristic acid.....	$C_{28}H_{48}O_4$	28	28	80
Benic acid.....	$C_{30}H_{50}O_4$	30	30	86
Cetyl or Palmitic acid..	$C_{32}H_{52}O_4$	32	32	92
Oxide of cetyl.....	$C_{32}H_{52}O$	32	32	96
Margaric acid.....	$C_{24}H_{44}O_4$	24	24	98
Stearic acid.....	$C_{26}H_{46}O_4$	26	26	104
Balenic acid.....	$C_{28}H_{48}O_4$	28	28	110
Arachidic acid.....	$C_{30}H_{50}O_4$	40	40	116
Behenic acid.....	$C_{32}H_{52}O_4$	42	42	122
Carotic acid.....	$C_{34}H_{54}O_4$	54	54	158
Oxide of ceryl.....	$C_{34}H_{54}O$	54	55	162
Melissic acid.....	$C_{36}H_{56}O_4$	60	60	176
Oxide of melissyle.....	$C_{36}H_{56}O$	60	61	180

This group includes the chief oily and fatty acids, as well as their aldehydes, which are omitted, and some oxides of the ethylic series. Glycerine is added, because these acids are always found in nature combined with it. The only two acids in which either part only of the oxygen of the carbonic acid, or the whole of it, without any from the water, has been separated, are the formic and acetic acids, which, accordingly, are powerful acids, soluble in water, and, though volatile, not oily. The rest are all oily or fatty, and become weaker as we rise in the scale, and in proportion as the oxygen of the water is more completely separated. The oxides of ethyle, methyle, amyle, cetyl, ceryl, and melissyle occur combined with acids of this series, forming compound ethers, to some of which the flavor of many fruits is to be ascribed. The acetate, butyrate, caproate, and caprylate of ethyle are found in the pineapple, melon, strawberry, &c. A similar salt of oxide of amyle gives flavor to the pear. Oil of gaultheria is the salicylate of methyle. Spermaceti is the cetylale of cetyl; and one kind of wax is the palmitate, another the cerotate, of oxide of ceryl.

GROUP VI.—Resins and Camphors.

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used. in eqs.	used. in eqs.	separated. in eqs.
Many resins.....	$C_{10}H_7O$	10	7	26
Camphor.....	$C_{10}H_8O$	10	8	27
Borneo camphor.....	$C_{20}H_{16}O_2$	20	18	56
Many resins.....	$C_{20}H_{14}O_2$	20	14	52
Many resinous acids.....	$C_{20}H_{14}O_2$	20	15	53

In this widely diffused group, very little oxygen is left. It includes an immense number of isomeric and polymeric resins and resinous acids. All are highly combustible.

GROUP VII.—*Carbohydrogens.*

Substance formed.		Carbonic acid	Water	Oxygen
Name.	Formula.	used in eqs.	used. in eqs.	separated. in eqs.
Oil of lemons, &c., &c.....	$C_8 H_8$	5	4	14
Oil of turpentine, &c., &c....	$C_{10} H_8$	10	8	28
Toluole.....	$C_{14} H_8$	14	8	36
Styrole (cinnamole).....	$C_{10} H_8$	16	8	40
Metastyrole (dracole).....	$C_{14} H_7$	14	7	35
Oil of juniper, &c., &c.....	$C_{15} H_{12}$	15	12	42
Cumole.....	$C_{15} H_{12}$	18	12	48
Cymole.....	$C_{20} H_{14}$	20	14	54

In this group, which is very widely diffused, the whole of the oxygen, both of the carbonic acid and of the water, has been separated, and consequently no further deoxidation can take place. Hence these compounds are very permanent, and are chiefly altered by their natural tendency to absorb oxygen under favorable circumstances.

It will be seen that these seven groups are so many successive steps in the scale of deoxidation, at one end of which stand carbonic acid and water, at the other the non-oxygenated essential oils. And it is evident also that the members of one group may be converted into those of the next higher by deoxidation, with or without the addition of water. This is probably what takes place, leaving out of view, for the present, nitrogen and sulphur. First, oxalic acid is formed; then malic, tartaric, and citric acids, &c., from it, or from each other; then sugar, starch, &c., from the acids; bitter, acrid, and colored compounds from sugar, starch, &c.; then oxygenated volatile oils; and then acids, perhaps also from sugar, &c.; then the oily and fatty acids, either from the preceding oils and acids or from sugar; then the resins, from the fats or from sugar; and, lastly, the carbohydrogens. Thus we have a picture of the whole process of vegetation, as far as concerns compounds devoid of nitrogen and sulphur; and we find it to be uniformly one of deoxidation. We shall find also that the same law holds in regard to all those products in which nitrogen and sulphur are present; but, before examining that subject, it may be remarked that the chief mass of plants is made up of woody fibre or cellulose, $C_{12} H_{10} O_{10}$, with starch, sugar, and gum, oils, resins, and fats, as well as vegetable acids, and that all of these are destitute of nitrogen. Hence the chief part of the food of plants is that which supplies carbon, hydrogen, and oxygen; in other words, carbonic acid and water.

These are supplied by the atmosphere. The various processes, constantly going on, of the decay of dead animals and vegetables, the respiration of animals, and combustion, are at every moment pouring carbonic acid into the air; and yet, in the free, open atmosphere, the proportion of carbonic acid never increases, as it would do in a closed space, beyond the average of $\frac{1}{10000}$ th, or a little more,

but never exceeding $\frac{1}{1000}$ th part of the volume of the air. Now, these processes not only produce carbonic acid, but also consume oxygen, and that in the same proportion, the oxygen they take up being equal in volume to the carbonic acid which it forms. And yet, not only does the proportion of carbonic acid in the air not increase, but that of the oxygen does not diminish. Evidently, therefore, some cause must be in operation, directly opposed to, and exactly balancing the processes of respiration, decay, and combustion. And such a process is that of vegetation, or the action of growing plants on carbonic acid and water under the influence of light, by which, as we have seen, these are deoxidised, vegetable products are formed, and oxygen is given out. Thus the air is kept in a state of purity, and yet is constantly undergoing change; for as fast as respiration, decay, and combustion consume oxygen and form carbonic acid, vegetation consumes carbonic acid, and produces oxygen. Any excess of carbonic acid instantly causes an increase of vegetation, and therefore of oxygen, as well as of food for animals. When animals by this food increase, they produce more carbonic acid, and so on, the oxygen circulating from the air to carbonic acid in the animal processes, and from carbonic acid, by means of plants, back to the air again.

It is quite conceivable, that in the earlier geological periods, when, as it appears, warm-blooded animals did not exist, the air may have been unfit for them, by reason of its containing too much carbonic acid. But this, within certain limits, would be favorable to vegetation, and especially, as there is reason to believe, to that of cryptogamous plants, such as ferns and lycopodiaceæ, and also the cycadaceæ. The action of such plants growing with enormous luxuriance, and not balanced by animal life, would in time diminish the amount of carbonic acid, increasing at the same time that of oxygen in the air, till it became fit for the respiration of warm-blooded animals, and the carbon, thus removed from the air, would be stored up in the form of remains of these plants, protected from decay by being covered with some rocky mass. In accordance with this idea, while the animals of the carbonaceous and other early periods seem to have been reptiles or fish, that is, such as required little oxygen, the vegetation, as found, partly decayed, in our coal-beds, seems to have been prodigiously luxuriant; and it is said that ferns and other similar plants, which abound in coal, really do grow most luxuriantly in an atmosphere charged with carbonic acid, to a much greater degree than air is. Be this as it may, vegetation would purify such an atmosphere, till warm-blooded animals and man could live in it; and then, the balance once attained, would continue undisturbed, as at the present day. In fact, air, taken from closed vessels, from the tombs of Egypt, 3000 years old, or the ruins of Herculaneum, 2000 years old, has been found as rich in oxygen as that of the present time.

Plants, then, obtain all their carbon, directly or indirectly, from the air: directly, by absorption through the leaves; indirectly, through the absorption of water by the roots, this water having dissolved some carbonic acid in passing through the air, and more in filtering through the soil, in which carbonic acid is constantly formed by the decay of organic matter. But this solution of carbonic acid has another and very important function to perform, namely, to dissolve earthy and alkaline phosphates and carbonates, and thus to supply the plant with its mineral food. Although, therefore, part of the wood, &c., of a plant may be formed from the carbonic acid entering by the roots, yet as plants give out from the roots a certain amount of carbon in the form of excretions, we find that the whole increase in the weight of carbon in a growing plant is really derived from the air by the leaves. The soil becomes richer in carbon rather than poorer, and thus the carbon of all crops, as far as its weight is concerned, comes from the air. There is no evidence that mould or humus ever enters the plant *as such*; but it is converted into carbonic acid, which enters by the roots and acts as a solvent for mineral salts. This, as we shall see, is the true reason why the presence of humus in the soil or in manure is advantageous. But direct experiments have proved, that plants can grow in perfection and produce fertile seeds, as the first plants must have done, in a soil destitute of humus or mould, provided it contain the necessary alkalies, phosphates, and other mineral salts, in a form adapted to entrance into the plant. In this case, the atmosphere easily supplies the whole of the carbon required, as well as the ammonia, if the necessary time be given.

Let us now attend to the nitrogen of plants. This, as already stated, is supplied to wild plants entirely by the air, and, so far as we know, only in the form of ammonia. Some authors have held that nitric acid furnishes nitrogen to plants, and that this acid is formed in the air by thunder-storms, and carried down by the rain, and they point to the occurrence of nitric acid in springs in proof of this. Now, it is true that nitric acid is formed in thunder-storms, but in very minute quantity, whereas ammonia is, and must be, present in the air at all times. When electric sparks are passed through air, nitric acid is formed, but a continuance of the sparks again decomposes it. Indeed, there is reason to believe that the nitric acid of storms is produced by the oxidation of ammonia of the air, as in nitrification, where ammonia is oxidised into nitric acid and water, $\text{N H}_3 + \text{O}_2 = \text{N O}_2, 3 \text{ H O}$; so that, even if nitric acid did yield nitrogen to plants, that nitrogen might be derived from ammonia. This would account, too, for the small amount of nitric acid formed. For if it were produced by the action of electricity on the nitrogen and oxygen of the air, there seems to be no reason why it should not be formed in very large quantity; while ammonia forms less than $\frac{1}{100000}$ th of the air, perhaps much less.

Nitric acid is chiefly found in springs where decaying organic matter is near them, as in towns, and is formed from the ammonia produced in their decay, by the same process as in nitrification. Besides, although plants probably possess the power of decomposing nitric acid, we know that many plants, such as tobacco and sunflower, actually produce nitric acid, or at least do not destroy that which enters them. On the whole, we may admit that both ammonia and nitric acid may yield nitrogen to plants, but we must not forget that nitric acid is most commonly formed from ammonia.

The origin of the ammonia in the air is obvious. It is contained in the excreta of animals, chiefly in their urine, and is also produced from the decay and putrefaction of dead animals and vegetables, the whole of their nitrogen rising into the air as carbonate of ammonia. The combustion of coal also yields it, and it is said that some ammonia is given out in the respiration or transpiration of animals. It is stated, that if the air of a crowded theatre be allowed to escape by a narrow opening above, while fresh air enters below, the air passing out is pungent from ammonia; but whether this be derived from the lungs or the skin is not known. But it is evident that the air must be continually receiving supplies of ammonia; and as plants cannot grow without it, and fix large quantities of it, they must be continually removing it from the air. Here, then, is a balance between vegetable life and animal life, supported by plants on the one hand, and decay on the other, similar to that above explained of the carbonic acid and oxygen; only the balance of nitrogen is single, while that of carbonic acid and oxygen is double. Ammonia, that is, its nitrogen, is taken up by plants, by them supplied to herbivorous animals, and by these to carnivorous animals; so that in this case vegetation and animal life act on the same side. And the decay or putrefaction or combustion of both vegetables and animals sends the whole of their nitrogen, in the form of ammonia, back to the atmosphere. This balance is as perfect as the former, and both combined keep the composition of the air perfectly uniform within certain limits.

The proportion of ammonia in the air is so small that it cannot be detected by direct tests applied to a small portion of air; but it is easily detected in rain-water by acidulating it with sulphuric acid, and evaporating it to $\frac{1}{300}$ th or $\frac{1}{400}$ th of its bulk. The addition of lime or potash will then set free ammonia, which may be recognised by its smell, and by forming white vapors with hydrochloric acid; or the addition of bichloride of platinum will cause a yellow precipitate of ammonio-chloride of platinum. It is evident that the ammonia of the air is brought to the soil by the rain, and enters plants partly by the roots, partly by the leaves; and it has been proved by experiment that the air is capable of supplying to plants, in the form of ammonia, all the nitrogen they require, provided only the soil contain the necessary mineral food in available forms,

and time be allowed. When we come to treat of manures, we shall speak of the uses of ammonia in them.

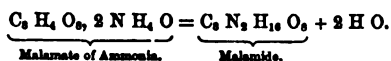
It will be as well to mention here, that the only remaining combustible or organic element of the food of plants, namely, sulphur (for the phosphorus is always in the incombustible form of phosphoric acid), is obtained from sulphates in the soil, chiefly sulphate of lime or gypsum, which serves to explain the value of gypsum as a manure.

We have seen how, in a general way, plants form, from carbonic acid and water, all those vegetable products which contain neither nitrogen nor sulphur, and invariably by the separation of oxygen. Now, to produce nitrogenised compounds, such as malamide or asparagine, indigo, and the vegetable bases, morphine, quinine, strychnine, caffeine, &c., it is only necessary that, to the conditions formerly mentioned, namely, an active cell, containing albuminous matter, and the presence of phosphates, alcalies, and salts, carbonic acid and water, sugar, &c., ammonia should be added; and the plant then, by the same process of deoxidation, gives rise to nitrogenised products. That these conditions are fulfilled is proved by the fact, that the juice of plants contains sugar or gum, albuminous matter, alcalies, phosphates, and salts, and among these, salts of ammonia. And it is easy to illustrate the formation of the compounds here alluded to. It must first, however, be mentioned, that ammonia, from its nature, is a very remarkable substance. It cannot be formed by the direct union of its elements, but only when they meet in the nascent state; and from the strong attractions of both its elements for other elements, it is particularly liable to transformations. Of these, the oxidation of both its elements, which occurs best in contact with bases, as in nitrification, has been mentioned. When ammonia is in contact with lime, air, and moisture, nitrate of lime is formed, and from this the nitrate of potash, $\text{N H}_3 + \text{Ca O} + \text{O}_2 = \text{Ca O, N}^2\text{O}_5 + 3 \text{H O}$. But in organic chemistry we meet with another peculiar transformation or series of transformations of ammonia, those, namely, in which one, two, or all three of its atoms of hydrogen are removed, in union with oxygen, derived from an acid; and both residues, the ammonia *minus* hydrogen, and the acid *minus* oxygen, combine to form new compounds, which are called amides, imides, and nitriles, according as the ammonia has lost one, two, or three atoms of hydrogen, and the acid, of course, one, two, or three atoms of oxygen. The simplest example of an amide is oxamide, formed as follows:

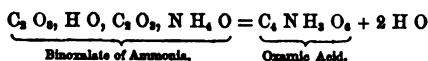
Oxalate of Ammonia.

Oxamide.

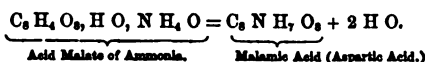
All amides are formed in the same way, by the separation of 2 eqs. of water from the neutral salt. If the acid be bibasic, the neutral salt contains of course 2 eqs. of ammonia; but here also, 2 eqs. of water are separated to yield the amide, as in asparagine or malamide.



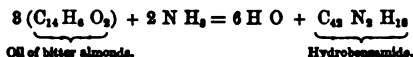
When the same change takes place in the acid salts of ammonia, with a monobasic or bibasic acid, the result is an acid amide. Thus binoxalate of ammonia yields oxamic acid.



and

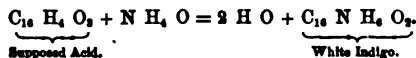


Thus the general law for amides, neutral and acid, is the elimination of 2 eqs. of water from a neutral or acid salt of ammonia. These amides are very numerous as artificial products, and one at least, malamide, or asparagine, is an important natural product. They all, when boiled with acids or bases, yield ammonia, and the acid from which they were formed. It is probable that amides have an important part to play in vegetation, and that they may contribute to the formation of vegetable bases. For in several instances, artificial amides are converted into bases, isomeric or polymeric with themselves. Thus, oil of bitter almonds, with ammonia, yields a neutral crystalline compound, hydrobenzamide,



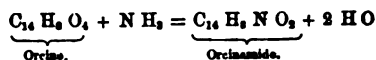
and this compound, when boiled with potash, is transformed into the isomeric base, amarine. In like manner, oil of bran, or furfurole, $C_{12} H_6 O_6$, with 1 eq. of ammonia, yields 3 eqs. of water, and 1 eq. furfuramide, $C_{12} N H_6 O_2$; and this, boiled with potash, is converted into the base furfurine, $C_{20} N_2 H_{12} O_6$, polymeric with it.

Under Indigo we have described colorless indigo, as it exists in the plant. This is probably an amide of an acid not yet known, $C_{16} H_4 O_2$. For

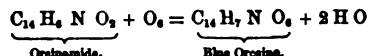


And this, when exposed to air, passes by the simple removal by oxidation of 1 eq. of hydrogen into blue indigo, $C_{16} N H_2 O_2$.

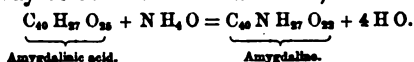
Some nitrogenous colors are produced by the combined action of ammonia and oxygen on colorless substances from plants, both processes going on outside of the plant, whereas in indigo the action of ammonia has taken place in the plant, and oxygen alone is wanting to produce the color. The beautiful dye archil is produced by the action of ammonia and air on the colorless oricine. Now, in this case, an amide is probably first formed, and afterwards oxidised.



and



Amygdaline, the peculiar bitter compound which yields the oil of bitter almonds, seems to be an amide of amygdalinic acid, an acid which may be obtained from it. Thus,



We may conclude, therefore, that all those compounds found in plants, which contain nitrogen without sulphur, are either amides, or derived from such compounds.

When a salt of ammonia loses so much water that 1 eq. of ammonia has lost 2 eqs. of hydrogen, and 1 eq. of the acid 2 eqs. of oxygen, the resulting compound is called an Imide, Imide being the name of the compound $N H$ which is left, as Amide is of $N H_2$. A few imides are known, but all are artificial, and, besides, they agree with amides in yielding the original acid and ammonia, when boiled with acids and bases. If they exist, therefore, in plants, they will be formed in the same way as amides, and yield analogous compounds. We need not, therefore, dwell on them. Were neutral oxalate of ammonia to lose 3 eqs. of water, instead of 2, it would yield oximide, $N H_4 O, C_2 O_3 = 3 H O + C_2 N H O$, which last would be oximide, differing from oxamide by 1 eq. of water.

The nitryles, which are compounds in which all the hydrogen of ammonia has separated as water with 3 eqs. of oxygen from the acid, are, for the most part, artificial products. Thus, benzoate of ammonia, $N H_4 O, C_{14} H_5 O_3$, if deprived of all its oxygen, that is, of the 3 eqs. in the anhydrous acid, and of the 1 eq. in the oxide of ammonium, along with 4 eqs. of hydrogen, 3 from the ammonia, and the fourth from the water which converts ammonia into the oxide of ammonium, and is necessary to the existence of all salts of ammonia with oxygen acids, yields *Benzonitryle*, $C_{14} N H_4$. It would appear that nitryles, which contain no oxygen so far as known, are derived from such acids as contain only 3 eqs. of oxygen when anhydrous, or 4 in the form of hydrate. Hence the acids of the Formic and Acetic series $(C_n H_{2n})_2 O_3$, readily yield nitryles, as well as those of the Benzoic series. The reader will observe, that in the equations above given for amides, the ammoniacal salts are represented with $N H_4 O$, when the acid is represented as anhydrous, and with $N H_3$, when the acid is given as hydrate. In all cases 1 eq. of water must be present, beyond the anhydrous acid and dry ammonia, $N H_3$, and it is of no consequence whether this be written along with the anhydrous acid, or with the ammonia, which it converts into oxide of ammonium, for $N H_3 + H O = N H_4 O$. It is there-

fore quite indifferent whether oxalate of ammonia be written, N H_2 , $\text{C}_2 \text{O}_3$, H O , or $\text{N H}_4 \text{O}$, $\text{C}_2 \text{O}_3$, and so for all similar cases. The fourth atom of hydrogen in $\text{N H}_4 \text{O}$, is always separated as water along with the other three, or with one or two of them. This is the reason why in the formation of amides 2 eqs., of imides 3 eqs., and of nitryles 4 eqs. of water are expelled from the neutral dry salt of ammonia. The oxalate of ammonia, as we have seen, yields oxamide by losing 2 eqs., and oximide, $\text{C}_2 \text{N H O}$, which would probably appear as cyanogen and water, by losing 3 eqs. of water; and if it lost 4 eqs., it would yield cyanogen, $\text{C}_2 \text{N}$, which is the oxalonitryle. Now there is a curious relation between the nitryles and cyanogen. For Formonitryle, $\text{C}_2 \text{N H}$, is hydrocyanic acid; Acetonitryle, $\text{C}_2 \text{N H}_2$, is the cyanide of methyle, and so on. Benzonitryle, $\text{C}_6 \text{N H}_2$, is probably the cyanide of phenyle, $\text{C}_6 \text{N}$, $\text{C}_{12} \text{H}_4$. It is not known whether all nitryles are cyanides, or whether some may not be isomeric with cyanides. We may conclude, therefore, that cyanogen and hydrocyanic acid, which occur in plants, are nitryles formed, the former from oxalate, the latter from formiate of ammonia. And it now appears, that some of the non-oxygenated volatile bases, such as nicotine and conine, are basic nitryles.

Having now explained the reaction of ammonia to form amides, imides, or nitryles, let us consider the formation of such compounds as contain nitrogen without sulphur, supposing them, as before, to be produced immediately, as we know they are mediately, from the food of plants—namely, carbonic acid, water, and ammonia. This will be best illustrated by a tabular arrangement.

Substance formed.		C O ₂	H O	N H ₃	O separated.
Name.	Formula.	used. in eqs.	used. in eqs.	used. in eqs.	in eqs.
Asparagine.....	$\text{C}_4 \text{N}_2 \text{H}_{10} \text{O}_6$	8	4	2	12
White indigo.....	$\text{C}_{16} \text{N H}_8 \text{O}_3$	16	8	1	33
Amygdaline.....	$\text{C}_{20} \text{N H}_{27} \text{O}_{22}$	40	24	1	82
Nicotine.....	$\text{C}_{10} \text{N}_2 \text{H}_{14}$	20	8	2	48
Coniine.....	$\text{C}_{16} \text{N H}_{18}$	16	12	1	44
Morphine.....	$\text{C}_{17} \text{N H}_{19} \text{O}_5$	35	16	1	80
Quinine.....	$\text{C}_{20} \text{N}_2 \text{H}_{24} \text{O}_4$	40	18	2	94
Strychnine.....	$\text{C}_{22} \text{N}_2 \text{H}_{22} \text{O}_4$	42	16	2	96
Caffeine.....	$\text{C}_8 \text{N}_4 \text{H}_{10} \text{O}_4$	16	0	4	28

The table will sufficiently illustrate the formation of the different classes of nitrogenised compounds which it embraces, namely, indifferent bodies, bitter compounds, coloring matters, volatile and fixed organic bases. They all contain very much less oxygen than the carbonic acid and water from which they have been derived, and some of them none at all. But there is no doubt that they are formed mediately, not immediately, and possibly from acids or sugar, acting on ammonia with deoxidation, the acids or sugar having been previously formed from carbonic acid and water by deoxidation.

There is a small but pretty widely diffused group of compounds containing sulphur, but no nitrogen. These are oils, and, like

almost all organic compounds of sulphur, they have a fetid alliaceous odor. Such are the oils of garlic, and probably of hops, of *Polygonum hydropiper* and of *Arum maculatum*. The only one yet analysed is the oil of garlic, $C_6 H_4 S$, which may be viewed as the sulphide of the radical *allyle* or *acryle*, $C_6 H_5$, isomeric, but not identical with propionyle, $C_6 H_5$, the radical of propionic or propylic acid. It is of course easily derived from 6 eqs. CO_2 , 5 eqs. H_2O , and 1 eq. SO_2 , for these, losing 20 eqs. of oxygen, would yield $C_6 H_4 S$. It is very probable that the oils of onions and leeks contain similar compounds, perhaps homologous ones, such as sulphide of formyle, $C_2 H_2 S$, or sulphide of acetyle, $C_4 H_2 S$, or sulphide of butyryle, $C_8 H_6 S$.

There is one remarkable oil, that of mustard, which contains both sulphur and nitrogen. It is, in fact, as has been already fully explained, the sulphocyanide of allyle or acryle, $C_6 H_5 + C_2 N S_2 = C_8 N H_5 S_2$, and it may be deduced from 8 eqs. CO_2 , 2 eqs. H_2O , 1 eq. NH_3 , and 2 eqs. SO_2 , simply by the loss of 24 eqs. of oxygen, or the whole oxygen they contain.

We now come to the most complex of all the organic products, namely, the albuminous or sanguigenous compounds, albumen, fibrine, and caseine, which are the highest in the vegetable scale, and the production of which, both as essential to the seeds, and as furnishing sanguigenous food for man and animals, is the chief object of vegetation. They contain, as we have seen, five combustible elements, carbon, hydrogen, nitrogen, oxygen, and sulphur, along with phosphates, essential to their existence. They cannot, therefore, be formed without a supply of phosphates, and as their presence is indispensable both to the cell and to its contents, plants cannot grow in a soil devoid of phosphates. In such a soil seeds will germinate and produce a few leaves at the expense of the seed, or of the first leaves, which die off. But here they stop, and however abundant the supply of carbonic acid, water, ammonia, sulphuric acid, silica, potash, common salt, lime, &c., yet if phosphoric acid be absent, the plant soon withers, without having produced seeds. When supplied with phosphates, plants grow vigorously and produce abundant fruit, and having done so, either die, or become torpid for the winter, after losing their leaves. So close is the connection between phosphates and sanguigenous matter, that the seeds, where the latter accumulate, yield, when burned, ashes formed chiefly, sometimes entirely, of phosphates; while the ashes of wood, straw, or leaves, contain chiefly carbonates and silica.

We have seen that these compounds are very complex, not only containing five organic elements, but containing a very large number of these in one molecule. Thus the smallest molecule indicated by analysis* contains of

* The formulæ here given to the sanguigenous bodies are not given as certain, but only as a near expression of the results of the best analyses. We have

	Carbon. Atoms.	Hydrogen. Atoms.	Nitrogen. Atoms.	Sulphur. Atoms.	Oxygen. Atoms.	Total. Atoms.
Albumen	216	169	27	2	68	482
Caseine	288	228	36	2	90	544
Fibrine	216	169	27	2	68	482

The fibrine in the table is vegetable fibrine, which agrees with that of flesh or sarcofibrine, in being apparently isomeric with vegetable albumen. (Blood fibrine or hemato-fibrine is said to be a different substance.) Now, we can easily suppose these bodies to be formed from sugar, $C_{12} H_{12} O_{12}$, that is, dry grape-sugar, along with ammonia and sulphuric acid. Thus :

Vegetable.	Employed.			Expelled.	
	Sugar.	Ammonia.	Sulphuric acid.	Water.	Oxygen.
Albumen and Fibrine..18		27	2	128	26
Caseine	24	36	2	168	36

Blood fibrine is not formed in vegetables, and is therefore omitted here. We can also easily deduce the formulæ of vegetable albumen and fibrine, and that of caseine, from carbonic acid, water, ammonia, and sulphuric acid, by deoxidation. In fact, the formation of sugar is only the first or early part of the process, supposed to occur before ammonia is concerned.

Vegetable.	Employed.			Expelled.	
	C O ₂	H O	N H ₃	S O ₂	Oxygen.
Albumen and Fibrine	216	83	27	2	454
Caseine	288	120	36	2	612

The following diagram will illustrate the process, viewed in two successive stages, the first being the formation of sugar.

	C.	N.	S.	H.	O.
216 eqs. carbonic acid	= 216				482
216 eqs. water	=			216	216
The sum is	= 216			216	648
Deduct 18 (C ₁₂ H ₁₂ O ₁₂) (sugar)	= 216			216	216
The difference is					482 eqs. of oxygen expelled in producing 18 eqs. of sugar.

already, in speaking of albumen, fibrine, &c., mentioned not only these formulæ, but more simple ones proposed by Hunt and others. The latter, however, agree less closely with analysis. It is certain only that the true formulæ are not yet known, but that they are very complex, and in the tables which follow, as well as others farther on, we merely use these formulæ for the purpose of illustration. Any others corresponding equally well with analysis, might be employed; but as no additional certainty has been obtained in regard to the true formulæ, those used in the last edition of this work are retained.

It is, however, necessary to remind the reader that caseine, which is here supposed to differ materially in composition from albumen and fibrine, is now believed by many to be isomeric with them in the combustible or organic part; in fact, to be albuminate of potash. But as this is still uncertain, the formula here given to caseine is left as it was.

	C.	H.	O.	
18 eqs. sugar $C_{12} H_{22} O_{11}$	= 216		216	216
Add 27 eqs. ammonia $N H_3$	=	27	81	
And 2 eqs. sulphuric acid $S O_3$	=		2	6
The sum is	= 216	27	2	297 222
Deduct 128 eqs. water $H O$	=		128	128 expelled.
	216	27	2	169 94
Deduct 26 eqs. oxygen	=			26 oxygen expelled.
Remains Albumen	= 216	27	2	169 68

Thus we see that if albumen be formed from sugar, there must be expelled 128 eqs. of water and 26 of oxygen; whereas, if it were formed immediately from carbonic acid and water, as explained in the second table, 454 eqs. of oxygen and no water would be given off. The reason of this is that albumen contains much less of hydrogen than of carbon, whereas sugar contains an equal amount of both, as well as of oxygen, and the excess of hydrogen in sugar must be given out in the form of water, while, if carbonic acid and water could directly yield albumen (with ammonia, &c.), only 88 eqs. of water would be necessary to 216 of carbonic acid and 27 of ammonia.

We have now traced the formation of all classes of vegetable products, and in doing so, two points are especially worthy of notice; first, that plants possess the power of building up, from comparatively simple molecules, such as are more complex, and that this complexity increases as we rise in the scale of vegetable products, till we come to those substances which form the vegetable tissue, such as woody fibre or cellulose (which is $C_{12} H_{10} O_{10}$, or perhaps a multiple of these numbers. The composition of starch, which is semi-organized, is the same as that of cellulose, $C_{12} H_{10} O_{10}$), and albumen, caseine, or fibrine, which are not only essential to the vegetable cell, but destined to form animal tissues, are greatly more complex even than this. Secondly, that in every part of the vegetable process, in the formation of every form of vegetable products, of acids, neutral bodies, cellulose, starch, fats, oils, resins, bases, and sanguigenous matters, one character universally prevails, that, namely, of deoxidation of the materials and liberation of the oxygen. When we deoxidise any substance in the laboratory, we do it by causing the oxygen to combine with another body; but vegetables, while they produce all matters essential to their own development and to the life of animals, give out, in doing so, the oxygen which is removed, and thus plants cannot grow without, as a necessity of their life, restoring to the air the oxygen withdrawn from it by the life of animals. We shall see that the chief processes going on in the animal body, which produce results equally varied and wonderful, are, in both the above points, of an opposite nature.

It would seem as if deoxidation were somehow favorable to the

coalescence of smaller molecules to form larger and more complex ones, for in almost all of those cases in which we have succeeded in building up, as the plant does, complex atoms from simpler, it is by deoxidation. But these cases are still few, and we have not yet learned to produce in this way natural vegetable products, apparently because we cannot yet imitate either the vegetable cell or the peculiar vegetable process of deoxidation; but are compelled to use coarser methods. We are more fortunate in the destruction or decomposition of complex organic products, for in this way, and especially by processes of oxidation, we have produced many substances identical with, and many others perfectly analogous to, vegetable products, but invariably less complex than the substances from which they are obtained. In this we imitate the destructive animal processes, while we fail to imitate the constructive process, whether of vegetable or animal life, the latter requiring the aid of the vital force to modify chemical action; the former depending chiefly, if not entirely, on chemical causes within our reach.

In vegetation water acts, not only by its elements, which are required, along with those of carbonic acid, ammonia, and sulphuric acid, to yield vegetable products, but also as a solvent for the essential mineral matters derived from the soil, all of which enter the plant, dissolved in water, or rather in a solution of carbonic acid in water.

Of these mineral substances, the most important are the alcalies, potash and soda; the alkaline earths, lime and magnesia; oxide of iron; silicic acid; chlorides of sodium and potassium; in sea-plants also the iodides of some metals; and the phosphates of lime and magnesia. It is as a solvent for lime, magnesia, oxide of iron, and the earthy phosphates and carbonates, that the carbonic acid taken up by the rain in passing through the air and the soil is so important; for all the other substances are soluble in pure water. And it is as a constant source of carbonic acid for this purpose in the soil that the presence of organic matter in the soil, or in the manure added to it, is so advantageous as experience shows it to be.

The alcalies and earth, oxide of iron, and silicic acid, found in fertile soils, are derived from the decay of rocks, and chiefly of felspar, the chief ingredient of granite, gneiss, mica slate, clay slate, hornblende rock, porphyry, greywacke, all slaty rocks, and all varieties of trap and volcanic formations. Many of these are very rapidly disintegrated, as some granites and slates, and the lava beds of Vesuvius, and yield at once a fertile soil. Others being more slowly acted on by the weather, yield soils of inferior quality, full of undecomposed felspar, which is quite insoluble. In such cases, the addition of quick or slacked lime has the effect of hastening the decomposition of the felspar, and rendering its elements soluble. This is the true explanation of the action of lime on stiff clay soils, which contain disintegrated, but not much decomposed felspar.

There is found on the sides of *Ætna* and *Hecla* a volcanic felspar rock, or one closely allied to felspar, which is called *Palagonite*. This is so readily decomposed, yielding abundance of soluble silica and of potash, the most essential elements (except the phosphates) of cereal crops, that it is actually used as a manure for poor soils, and will ere long be imported into other countries for that purpose. The fertility of soils, *ceteris paribus*, depends on the proportion of decomposed felspar, or of such as is annually brought by the weather into the soluble form. The chief benefit derived from frequent ploughing, especially in stiff soils, is that it promotes the access of air and moisture, and thus hastens the decomposition of the felspar. The burning or calcination of stiff clay has the same effect; for calcined felspar is much more easily acted on by the air than it would have been previous to calcination.

Common salt is found everywhere, in every spring, and in every soil. Sulphate of lime or gypsum, which yields to plants their sulphur, is also very generally diffused in soils and in water, in which it is soluble. The quantity of gypsum in many soils is so large, that no benefit can be derived from the addition of it as manure, and the farmer who adds it in such cases, simply wastes the price of the gypsum. But where it is absent, or present only in small proportion, then the addition of gypsum produces wonderful results.

The phosphates, which are absolutely indispensable to the growth of all vegetables, are found, fortunately for mankind, universally diffused both in rocks and in soils. There are few rocks, such as granite, greywacke, &c., in which minute scattered crystals of *apatite* or phosphate of lime may not be seen with the aid of a microscope; and the phosphates are present in every soil on which vegetation is found. The volcanic beds, which yield such fertile soils, are particularly rich in phosphates, and these salts also occur in many limestones (all of which have had an animal origin, as seen in shell marble, shell limestone, and chalk, which are often entirely formed of shells), in considerable quantity. Such limestones are of course the best for the farmer. But, on an average, the proportion of phosphates in any soil is so small, that one, or at most a few good crops, exhaust it, or nearly so; that is, they exhaust the available supply of phosphates, &c. There are soils, such as those of *Vesuvius*, of certain districts on the lower Danube, and of great part of the United States, which either have not been exhausted by centuries of cropping of wheat or tobacco, or have only become exhausted after 100 or 200 years of annual crops of the richest kind. But ordinary soils are comparatively poor, and hence the necessity for manure, that is, for restoring to the soil what has been removed in the crop, especially the phosphates and alcalies, the ingredients most easily exhausted. The excreta of animals, solid and liquid, being rich in these substances, are the best manure; because they contain the phosphates and alcalies in the proportions required for plants, and

also in the proper forms, since they are derived from the plants on which the animals have fed, and are, indeed, nothing else than the ashes of those plants. But farm-yard manure is not valuable only as containing phosphates, but also as containing ammonia or sources of ammonia, and organic matter, which serves as a source of carbonic acid. The most essential elements of manure are the phosphates and carbonaceous matters; for the latter supply a solvent, carbonic acid, for the phosphates both of the manure and of the soil; and if this solvent be supplied, and the soil or manure supply also phosphates, alcalies, and sulphates, the air will furnish ammonia, *provided time be given*. This has been practically demonstrated on a large scale by Liebig, who, by manuring a barren and worthless soil with phosphates, alcalies, silica, and sulphates alone, obtained excellent results with wood and other perennial crops; but found the result less favorable with cereals and other annual crops, which require a large supply of phosphates in a short time. He next added to the mineral manure sawdust, to yield carbonic acid, and now he obtained excellent results even for annual crops, although no ammonia was added, and the atmosphere supplied all the nitrogen. But it is certain that when the supply of phosphates is rapid, as it was here from the solvent action of the decaying sawdust, the air can supply any amount of ammonia, which cannot be assimilated without abundance of phosphates. The further addition of ammonia to the mineral manure and sawdust brought it to the state of farm-yard manure, and then the same result is obtained in a still shorter time—a point of much importance in temperate or cold climates. Of course, to render, as in this experiment, barren soil fertile, is an expensive process, from the necessity of adding to it so great an amount of mineral matter. But wherever a sufficient quantity can be added to it, without raising the cost of the improved barren soil to or above that of fertile soil, then, by the judicious cropping and manuring of the improved land, its artificial fertility, like that of a soil originally fertile, may be kept up from its own produce, aided by the action of the weather, and if economically procurable, by liming.

Farm-yard manure, solid and liquid together, is the standard or model manure, and the object of all artificial manures is, in part or in whole, to imitate or replace it. The best sources of phosphates, next to farm-yard manure, are bone-dust and guano. Bone-dust is composed of phosphates and gelatine. Guano is the decaying residue of the excrements of sea-fowl fed on fish, and contains phosphates and salts of ammonia, with some carbonaceous matter. It is evident that both resemble farm-yard manure, more or less, and that both are deduced, like it, from the vegetable food of animals; for the fish consumed by the sea-fowl fed on other fish, which fed on animalculæ, which fed on sea-plants. Another valuable source of phosphates is that of beds of phosphate of lime, derived from ex

tinct animals. There are such beds, of vast extent, in Spain : others have been found near the Rhine, and in Canada ; and beds more or less entirely composed of coprolites, the fossil excrements of fish and reptiles, fed on other animals, are abundant in England, as well as in other countries. These may be called fossil guano, and only differ from recent guano in having lost their ammonia and carbon. All these are extremely valuable as manures.

But we must never forget that the best and most economical of all manures, is farm-yard manure, or, what is the same thing, the night-soil and urine of inhabited places. In large cities, the amount of this invaluable matter is prodigious ; it represents, in fact, as far as phosphates go, the whole food of the inhabitants ; and yet, from ignorance or carelessness, the greater part of it is wantonly cast into the sea, from which a mere fraction is, at a great expense, recovered as fish and guano. There are, no doubt, some practical difficulties in the way of saving the whole of the contents of our sewers in large cities ; the chief of which is, the enormous amount of water added to them in order to wash them away from our habitations. But the subject has at length been taken up in earnest, and there are no difficulties which may not be overcome. The bone-dust we import at a high cost, from other countries, is lost to them, and is to us only a circuitous mode of recovering a small part of what we have thrown away. In process of time, no nation will consent to sell bone-dust, save at a price which will render its use impossible ; and we must come to that to which the Chinese, with their practical sagacity, have come many centuries ago, namely, the principle of restoring to the land every thing that is taken from it in the crops ; the only principle on which agriculture can be permanently or profitably conducted on average soils. The amount of phosphates in our edible crops is far beyond any thing ever seen in natural wild-plants ; and, therefore, the supply required by a dense population, and obtained in the excessive development of seeds and roots in cultivated plants, must be given to the soil in the shape of manure, the best being that derived from man, who consumes the crops. The rotation of crops, which takes advantage of the fact that one crop requires more of one ingredient and less of some other than another crop does, and the occasional use of fallow, which allows the weather to act, and to render soluble a fresh supply of mineral matter, are only different branches of the best method of following out the great principle of agriculture above enunciated. The cereals and grass require more silica ; turnips and potatoes more of the alcalies ; peas, beans, clover, and other leguminosæ, more lime and sulphates ; and thus may be alternated with great advantage, although all require a full supply of phosphates. For details on these important subjects, which our space forbids us to enter upon more fully, but the principle of which we have endeavored to explain, the reader is referred to Liebig's *Agricultural Chemistry*, to the third edition of his *Letters on*

Chemistry, and to a small work recently published by him, the "Principles of Agricultural Chemistry."*

A mistake is often made in the use of artificial manures, which is caused by ignorance of the principles on which they act. The farmer has added guano, bone-dust, or gypsum, and has obtained a very heavy crop. He repeats the dose, and a failure ensues. The reason is, that the first addition had enabled the crop to assimilate all the available alcalies, silica, or sulphates present in the soil, or the greater part of them, so that, on the second addition of phosphates, there was a great deficiency of one, or another, or of all these matters; and as all are equally essential, the deficiency of any will cause failure. On restoring the balance, success will again be the result. Good farm-yard manure is the only one not liable to this cause of failure, because it is the only complete manure; the others being more or less partial, or confined to one substance. Of course the same risk of failure exists, if the artificial manure added at first with success has been potash, or salts of ammonia; for the addition of any of these, if previously deficient on the soil, will enable the crop to take up a large proportion of the others, or of phosphates, and may exhaust it of any one for the time. This ought particularly to be attended to, as when special manure acts, it does so by exhausting the soil, *pro tanto*, of all the *other* necessary mineral ingredients.

The ashes of wood, peat, or coal, are valuable as manure, containing the mineral elements of wood, and of those plants from which peat and coal have been formed; mixed, in coal, with clay and sand. The ashes of straw are very valuable, especially for grass or the straw of corn. In general, the ashes of any crop are the best mineral manure for that plant. The burning of heath, or of the turf pared from moorland soil, is useful in two ways: first, by the action of heat on the felspar in the soil; secondly, by supplying the ashes. By examining the ashes of the plants which grow naturally on any soil, we can easily discover what are the most valuable constituents of that soil, and thus judge of the proper addition to it. The ashes of any crop are identical with the ashes of the excreta of the animals fed on that crop.

The addition of ammonia to any soil, in the manure, can only be of use in so far as that soil contains, in an available form, a due proportion of alcalies, silica, phosphates, common salt, oxide of iron, and sulphates; and the same is true of every special manure. A soil, if totally deficient in any one necessary ingredient, will be absolutely barren. Thus, if all the other matters be present, and phosphates, or sulphates, or alcalies be alone absent, no plant can grow there; but the addition of the ingredient which is wanting will convert the soil into a very fertile one. If a soil be fertile for turnips

* Walton and Maberly, London.

or potatoes, and will not yield corn or hay, it is deficient in soluble silica, essential to straw. If a soil yield grass and straw, but not corn, as sometimes happens, this may arise from deficiency of magnesia, which, in the form of phosphate, is essential to the husk of grain, so that in its absence no perfect seed is formed. Bran and urine, which both contain phosphate of magnesia, are on that account, and on many others, very valuable for corn. A soil on which corn grows, while clover or peas do not, is probably deficient in available lime or in gypsum. But in some plants the absence of one base may be supplied by another, potash by soda, lime by magnesia. When a soil is deficient in most, or in all, of the necessary mineral matters so often mentioned, it is hopelessly barren. Such is the case with the soil of districts where quartz rock prevails, or where the soil has been derived from that rock, as is seen in part of the northwest of Ireland. But happily such soils are rare, because such rocks are rare in any great extent. The deserts of Asia and Africa are barren, not because the soil is devoid of the mineral food of plants, but because of the want of water. Even in the desert, every spring is surrounded by an oasis of vegetation.

We have said that the presence of decaying organic matter in the soil is useful in two ways; as a source of carbonic acid, which principally acts, dissolved in water, as a solvent for lime, magnesia, and phosphates; and as a source of ammonia. Both of these enable the plant to assimilate the necessary mineral matter in a far shorter time than it could without them; and this is a point of very great importance in our climate, where the summer is short, compared to that of tropical regions. To illustrate the power of water containing carbonic acid to dissolve phosphate of lime, insoluble in pure water, I may state that I found the carcase of a pig, buried on the slope of a hill, which was moist and undrained, when taken up after fourteen years, to have shrunk into a flat cake (the change, most probably, had been effected in a much shorter time), which was entirely composed of fatty acids from the fat of the animal. The muscles and membranes, nerves and vessels, had putrefied and disappeared, and not a trace of bone-earth was to be found. The whole had been dissolved by the water percolating through the body, and had thus been carried down to the lower ground. I found the water, like all water that passes through soils, to contain carbonic acid, and this had been the solvent. Hence, if cemeteries are placed in a high situation, the bone-earth is rapidly carried down to the valleys in a moist climate. In a dry situation, bones remain unaltered for centuries, as in the sandy soil of the field of Cannæ, on which the bones of those killed in that battle are often found to this day entire, though having lost much of their animal matter. The solvent power of carbonic acid must act in every soil, and hence the value of humus on the soil and of decaying organic matter in manure.

We have now examined the process of vegetation, its results, and its indispensable conditions. It is perhaps worth while to remind the reader of the very important part played by the solar rays in vegetation. That essential process, by which the plant decomposes carbonic acid and water, liberating their oxygen, can only take place under the influence of luminous rays; for although, on the prevalent undulation theory, heat and light are both regarded as vibrations of the same kind, only differing in velocity, light only appearing when the vibrations amount from 400 to 800 billions in a second, and non-luminous heat when they fall short of 400 billions in a second,—although, therefore, light and heat are both motion, yet non-luminous heat cannot enable a plant to decompose carbonic acid and water. Now, if we consider that the chemical effect of light, light being motion, is a mechanical effect, and that the mechanical power necessary to decompose carbonic acid and water is enormous, we see that the amount of mechanical effect produced in growing vegetables by the solar rays must be very great indeed. In fact, it has been calculated that the mechanical force derived from the sun by the amount of wood growing in a year on one square foot of surface corresponds to that which would be required to raise a weight of 486,000 lbs. to the height of one foot; and this is only $\frac{1}{17}$ th of the whole effect of the sun's rays, of which only $\frac{1}{2}$ th reaches the plant, and half of that is lost. The recent investigations of Carnot, Joule, W. Thomson, and others on the relations of heat, light, and mechanical effect, tend, indeed, to show that all the mechanical effect (except in a few cases, such as water and tide mills, volcanic action, and a few more), which is available to man, is derived from the solar rays, directly or indirectly. We have seen that a vast amount is expended in producing vegetables, and it is obvious that the whole mechanical power of the animal body is drawn, mediately or immediately, from that which has been stored up in plants; while the power of the steam-engine is derived from the conversion into heat of the mechanical force stored up in the fuel, whether wood or coal. This force, as we have seen, proceeds directly from the solar rays.

Vegetables, as we have seen, cannot possibly grow and form seeds, without at the same time producing, as parts of their own structure, the food of animals in its two great forms, of non-nitrogenous or respiratory food, namely, starch, sugar, gum, and oils; and nitrogenous, plastic, or sanguigenous food, namely, albumen, fibrine, and caseine. The former, which do not enter into the formation of blood, save, to a small extent, oils or fats, may exist free from ashes or mineral matter, although these are necessary to their production; but the latter cannot exist, in the organism, at least, without containing at all events phosphates. And thus, by the beautiful arrangement which renders albumen, fibrine, and caseine indispensable to the development of plants, and to the production even of

starch, sugar, and fat; and which has rendered the presence of phosphates indispensable to the existence of albumen, fibrine, and caseine; vegetables cannot grow, nor produce the plastic food of animals, or that which yields blood, without at the same time producing, and supplying to animals, the earthy matter required for their bones, and in a smaller proportion, for the blood and for all the tissues. If albumen, &c., could be formed without phosphates, or if even blood and muscle could exist without phosphates, still animals could not exist or be formed without bone-earth. As it has been arranged with perfect wisdom, however, the mere fact that a plant has grown, necessarily implies that it contains the materials required to support animal life, provided, of course, it be not a poisonous plant, and probably there is no plant which may not serve as food for some animal.

The food of animals, then, consists of respiratory and sanguigenous matter. It is first masticated and mixed with the saliva, which includes in its viscid substance a quantity of air. It is then introduced into the stomach, where digestion takes place. The saliva, which is alkaline, and contains a peculiar modification of albumen, called ptyaline, has a peculiar power, not possessed by the gastric juice, of converting starch into sugar, which is an essential part of digestion. It also conveys oxygen, in the form of inclosed air, to the stomach, where the oxygen probably assists in producing the peculiar change in the gastric juice, or in the epithelial matter suspended in it, by which the gastric juice dissolves albumen, fibrine, or caseine. The gastric juice, which is acid, and contains phosphoric, lactic, and hydrochloric acids, has the very remarkable property of dissolving coagulated albumen, as well as fibrine and caseine, at the temperature of the body, but has no action on starch. Since it acts as well after filtration as before, it is probable that the ferment it contains is a dissolved one, and not, as Frerichs states, suspended epithelial cells.

When the food has been digested to a certain extent, it leaves the stomach, and enters the intestines, where it is soon after mixed with the bile. It is also continually mixed with the intestinal secretion, a fluid which is viscid, alkaline, and contains no albumen. It possesses, however, both the power of the saliva to dissolve starch as sugar, and that of the gastric juice to dissolve sanguigenous matter, and it evidently contributes to the completion of the digestion of the starch and albumen, &c., of the food. The bile, as has been proved, is nearly all reabsorbed in its passage through the intestines; and the pancreatic juice, which also mixes with the food, has been said by Bernard to be the agent of the solution of fat or oil, which it is said to convert into an emulsion, capable of entering the absorbents. It is certain that the pancreatic juice can resolve neutral fat oils into glycerine and fatty acids, and that this action is prevented by the gastric juice, and favored by bile. But the latest re-

searches tend to prove that the means by which fat is absorbed are not yet known, although the bile and pancreatic juice, especially the bile, in some way contribute to it. Oil is not absorbed by diffusion or endosmosis, nor are the fatty acids, when separated; and the absorbed fat is neutral. Whatever be the means, the fat, if not exceeding a certain amount, is certainly absorbed, and thus, when the food has passed through the stomach and intestines, all the starch, albumen, &c., and fat, has been taken up, as well as nearly the whole of the bile. The insoluble residue, or *fæces*, consists of woody fibre, a little coloring matter, supposed to come from bile, and the insoluble earthy salts of the food, as well as of the effete tissues, while the soluble salts, entering the circulation, are expelled in the urine.

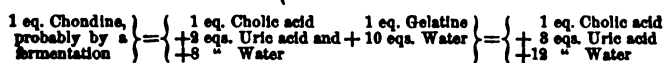
The fibrine and caseine of the food appear in the dissolved food, or chyle, almost entirely as albumen, along with the albumen of the food; and it would seem that albumen, in the blood, as in the egg, is the true source of the tissues. Chyle contains very little fibrine, and blood only about 1 or 2 parts in 1000, and there is reason to think that fibrine is rather, in the blood, a product of the destruction of the tissues, than a substance from which they are formed. The chyle, along with the lymph, is mixed with the blood and passes through the lungs, where it probably acquires its color. The red corpuscles of the blood are nucleated cells, or rather the nuclei of such cells, which abound, in a colorless form, in lymph, and are even found without color in the blood, especially in a diseased state. The blood is the most complex of all fluids, containing not only the food of all the tissues, but the products of their oxidation. For in the lungs the venous blood takes up oxygen, and gives out carbonic acid. It then goes, as arterial blood, to the heart, whence it is sent to every part of the body, carrying with it the oxygen, which it gradually exchanges for carbonic acid, formed by the oxidation of the tissues, but, as the products of oxidation are constantly removed from it by the excretory and secretory organs, they are always in small proportion. In this brief sketch we have not alluded to the presence of glucose in the blood and liver, because the subject is still but little understood. But under the blood we have mentioned that the glucose is transformed into lactic acid, which is oxidised and burnt off in the blood.

Let us now endeavor to follow some of the changes, first in digestion, and then in the circulation. The reader will bear in mind that

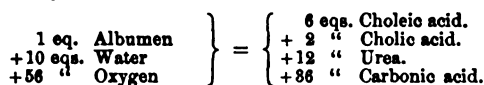
Vegetable albumen, and vegetable fibrine,	} are isomeric with {	Albumen of blood	} all being $C_{214} N_{37}$ $S_4 H_{100} O_{30}$.
		Albumen of flesh Fibrine of flesh	

Consequently, when vegetable albumen and fibrine are digested into animal albumen, we may call it an isomeric transmutation. But when caseine, which is $C_{268} N_{44} S_4 H_{228} O_{90}$, is digested, it yields albumen and chondrine. Thus:

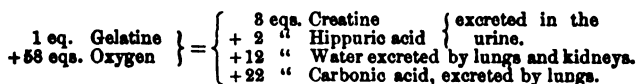
Here we find that every one of the above changes is one of oxidation, and that, as it proceeds farther, we come to the constituents of the urine, and to carbonic acid. This, then, is the characteristic feature of the changes in the animal body. As long as albumen is to be formed, and even, to a certain extent, in the formation of gelatine and chondrine, these three bodies being the chief materials of the tissues, the addition of water alone suffices; but when oxygen comes into play, the changes strike deeper, and we obtain the constituents of bile and of urine, as well as carbonic acid, to be excreted by the lungs. When gelatine and chondrine have formed part of tissues, they, like albumen, become effete, and must be decomposed and removed. We have then:



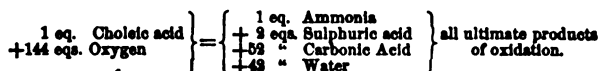
And we may also have, with albumen,



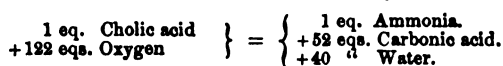
There are certainly many intermediate stages, but of these little is known. One, however, may be mentioned as probable, namely, the production from gelatine of creatine, hippuric acid, water, and carbonic acid. Thus,



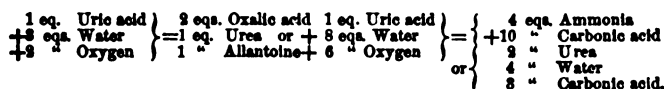
Again, choleic acid fully oxidised will yield as follows:



Cholic acid, which contains no sulphur, will yield



When uric acid is produced, in warm-blooded animals, but a small part of it reaches the urine; because, from their structure, only soluble compounds can be excreted through the kidneys, ureters, bladder, and urethra. The uric acid is therefore further oxidised; and



In this manner the insoluble uric acid is converted, by oxidation, into soluble products. Oxalic acid is obviously the result of imper-

fect oxidation, and meeting with lime in the bladder, forms the oxalate of lime or mulberry calculus. Allantoine, also a product of imperfect oxidation, is found in the allantoic fluid, the urine of the fetal animal, and in that of very young animals. With full oxidation of the uric acid, only urea, water and carbonic acid, or ammonia and carbonic acid, are formed. The ammonia, if in excess, throws down earthy phosphates in the bladder, and thus gives rise to the phosphatic calculi. The uric acid calculi, the commonest of all, depend on the deficiency of oxygen, or what is the same thing, excess of sanguigenous, and particularly of gelatinous food, as well as on sedentary habits, which diminish the amount of inspired air; and lastly, on deficiency of alkalies, the presence of which is necessary to promote the oxidation of the uric acid.

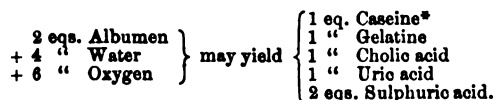
In the changes we have thus briefly described, by which the tissues are wasted, the nitrogen of these tissues takes ultimately the form of urea, and thus the quantity of urea secreted in a certain time is a measure of the amount of change or waste of matter in the system. An adult man secretes, on an average, about 463 grains of urea, or rather more than 1 ounce avoirdupois in 24 hours. The quantity of uric acid in normal urine is so small in comparison that it hardly amounts to $\frac{1}{1000}$ of the weight of the urea, and may therefore be neglected.

It has been proposed to observe and record the daily secretion of urea in health and disease, as an important fact in physiology and pathology, and for this purpose various methods have been proposed for determining the percentage of urea in urine directly and quickly. Perhaps the best is that of Liebig, which is founded on the fact, that urea forms with peroxide of mercury a white compound, insoluble in water. He employs a neutral and diluted solution of permanganate of mercury, of known strength. This is added to a known volume of urine as long as it causes a white precipitate. But as the nitric acid set free prevents the complete precipitation, the liquid is now neutralised exactly by baryta water, and the permanganate now causes a further white precipitate. These operations are repeated, until at last a yellow precipitate begins to appear, which is a proof that all the urea is precipitated. The volume of permanganate employed being known, and previous experiments having ascertained how much urea is precipitated by 100 volumes of it, it is easy to calculate the urea present in the urine under examination.

Another form of this process is as follows. To the urine is added half its volume of a mixture of equal parts of the saturated cold solutions of hydrate of baryta and nitrate of baryta, which precipitates the whole of the sulphuric and phosphoric acids present. To the filtered liquid the neutral and diluted solution of permanganate of mercury of known strength is added by degrees, until a drop of the liquid, tested with carbonate of soda, gives a yellow precipitate, which shows that a slight excess of permanganate has been added.

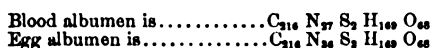
In either case if any given volume of urine, say 10 cubic inches, requires 30 cubic inches of the normal solution of pernitrate, and if we have made this normal solution of such strength that 1 cubic inch of it corresponds to 1 grain of urea, then the 30 cubic inches employed will indicate 30 grains of urea in the 10 cubic inches of urine.

We have now to attend to the formation of caseine (in milk) from albumen or fibrine, isomeric with it, in the animal body. This change, like the others, depends in some degree on oxidation.

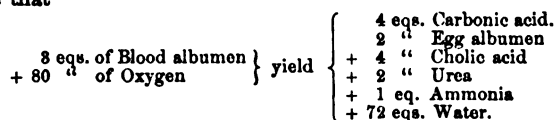


2 eqs. of albumen are necessary to yield one of caseine, because the latter compound contains more carbon, hydrogen, nitrogen, and oxygen than the former. We have already seen that when caseine, in the young animal, yields albumen, it also yields chondrine, these being the two substances most necessary for the young animal. Here we see that when milk is formed in the mother's body, it is accompanied by gelatine, cholic acid, uric acid, and sulphuric acid, to be employed in her own organism.

Let us now consider the albumen of eggs, which differs from that of blood, as follows :



The difference is 9 eqs. of nitrogen and 1 of sulphur more in egg albumen than in blood albumen. In the body of the fowl we may suppose that



And during incubation, or in the stomach or circulation of an animal,



Of course fat and oxygen may supply the place of sugar, since, as we shall see, fat is sugar *minus* oxygen. Now, the yolk of egg is rich in fat, and is said also to contain sugar; while the food of animals, in addition to eggs, when they are used, always contains starch, sugar, or fat. And it is quite certain, that all the tissues are formed in the egg from egg albumen and the oil or sugar of the yolk, aided

* It has been stated, that caseine is possibly the albuminate of potash.

by oxygen ; as also, that in the animal body, all the tissues may be formed, or blood produced, from eggs, especially with starch, sugar, or fat.

We have now considered, as fully as our space permits, the relations of the sanguigenous compounds to each other, and to the tissues, and we have seen that these compounds are formed in plants, and that in animals they are mutually convertible, sometimes by an isomeric transmutation, as when fibrine is dissolved into albumen—a process capable of being imitated out of the body, and at the other times with the aid of water, or of water and oxygen. In no case is free oxygen given out, as in plants ; but the final result is, that the oxygen taken up in the lungs is given out as carbonic acid and water.

We have not entered into details as to the coloring matter of the blood or hematosine. This is albuminous, and contains iron. Hence the use of iron in the food. We do not know its exact composition, nor where it is formed. But we do know that the purest and whitest blood fibrine also contains iron, and hence possibly one function of this hemato-fibrine is to yield the material for hematosine.

There remains one more substance, which certainly assists mechanically in the formation of tissues, and probably is essential to the production of cells and of blood corpuscles. This is fat, which we have seen to be non-nitrogenous, and to be formed abundantly in the vegetable kingdom. Many kinds of food contain fat or oil ready formed, and, as we have seen, it enters the blood in some obscure way, to which the bile and probably the pancreatic juice contribute. It is never absent from blood. But fat, which is not a sanguigenous compound, can also be produced from starch and sugar in the animal body. The bee forms wax, a true fat, from honey ; and animals abundantly fed with grain, which contains only traces of fat, and so situated as to suffer from deficiency of oxygen, become rapidly loaded with fat. Thus ortolans, when kept in confinement, which reduces their respiration, and in the dark, which leads them to feed voraciously, by a natural instinct, on the admission of light, may thus be led to feed many times a day on grain, and rapidly become absolute balls of fat. When geese are prevented from moving, and crammed with maize or wheat, their livers become so charged with fat as finally to be unfit for their proper functions, and greatly enlarged. And stall-fed cattle are notoriously much fatter than such as have to travel far in search of food, while wild animals are almost always lean.

These facts prove that fat is formed from starch, which first becomes sugar, in the animal body. In this particular the animal resembles the plant ; but in the animal, the oxygen separated from sugar to convert it into fat, is not given out, as in the plant. It is either at once converted into carbonic acid and water, or added to the oxygen taken up from the air, and used for the same purposes. Thus we see that the power of the animal to deoxidise sugar, which he employs when oxygen from the air is deficient, supplies that defi-

ciency. To illustrate this, the reader must be reminded that fats and fat oils are compounds of oxide of glyceryle or oxide of lipyle, $C_3 H_7 O_2$, or $C_2 H_5 O$, with fatty or oily acids, chiefly of the series $(C_n H_{2n})_2 O_2$. Such a neutral fat, consisting of margaric acid and oxide of lipyle, is the chief ingredient of human fat, and is called margarine. If the acid be oleic acid, the fat is called oleine; if the acid be butyric acid, butyrine, and so on. Now, every fatty or oily acid, as well as oxide of lipyle, may be derived from sugar by deoxidation, and in the case of oleic acid, $C_{18} H_{34} O_2$, and oxide of lipyle, $C_3 H_7 O_2$, both of which contain an excess of carbon over hydrogen, by deoxidation and loss of water. Thus:

- 1 eq. Sugar $C_{12} H_{22} O_{11}$, losing 4 eqs. of oxygen, yields 2 eqs. propylic acid = $2 (C_3 H_7 O_2)$.
 1 eq. Sugar $C_{12} H_{22} O_{11}$, losing 4 eqs. of oxygen and 4 eqs. of water, yields 2 eqs. oxide of lipyle = $2 (C_3 H_7 O_2)$.
 8 eqs. Sugar $C_{24} H_{46} O_{22}$, losing 32 eqs. of oxygen, yield 1 eq. stearic acid = $C_{18} H_{34} O_2$.
 8 eqs. Sugar $C_{24} H_{46} O_{22}$, losing 30 eqs. of oxygen and 2 eqs. of water, yield 1 eq. oleic acid = $C_{18} H_{34} O_2$.
 17 eqs. Sugar $17 (C_{12} H_{22} O_{11})$, losing 180 eqs. of oxygen, yield 6 eqs. margaric acid = $6 (C_{24} H_{46} O_{22})$.

This table suffices to show that all fatty acids of the acetic series, such as propylic, margaric, and stearic acids, are derived from sugar by simple deoxidation, and that oleic acid and oxide of lipyle are derived from sugar by the loss of oxygen and water. Let us now take one fat, margarine, which is composed of margaric acid and oxide of lipyle.

Sugar.	Margaric acid.	Oxide of lipyle.	Oxygen.	Water.
17 eqs. yield	6		180	
8 eqs. yield		6	12	12
Consequently 20 eqs. yield	6	6	192	12
	6 eqs. Margarine.			

that is, 6 eqs. of margarine, 12 of water, and 192 of oxygen.

Let us now revert to the oxidation of albumen, and we find that

$$\begin{array}{l}
 \left. \begin{array}{l} 4 \text{ eqs. Albumen} \\ 40 \text{ " Water} \\ + 224 \text{ " Oxygen} \\ \text{from the air} \end{array} \right\} - \left. \begin{array}{l} 4 \text{ eqs. Choleic acid} \\ 8 \text{ " Choleic acid} \\ 12 \text{ " Urea} \\ + 26 \text{ " Carbonic acid} \end{array} \right\} - \left. \begin{array}{l} 4 \text{ eqs. Albumen} \\ 40 \text{ " Water} \\ 32 \text{ " Oxygen from the air} \\ + 192 \text{ " Oxygen} \\ 6 \text{ " Margarine} \\ 12 \text{ " Water} \end{array} \right\} = 20 \text{ eqs. sugar}
 \end{array}$$

Here we see that on the left hand the albumen is oxidised by the air alone, but on the right hand is represented as unable to obtain more than 32 eqs. of oxygen, out of 224 that it requires from the air, and as procuring the remainder from 20 eqs. of sugar, which, yielding 192 of oxygen, form, at the same time, 6 eqs. of margarine or fat, and 12 of water. This proves that the formation of fat from sugar in the animal body, which certainly takes place, is a source whence the blood may obtain oxygen when respiration is impeded. Were it not for this, an animal kept from free motion would soon

die from the accumulation of unoxidised matters in the blood. Instead of dying, the animal lives; but, if supplied with starch in his food, obtains the oxygen necessary for the change of matter in the vital processes from the starch or sugar, and in doing so necessarily becomes fat.

There is another process by which fat may be formed in the body, and which does not, like this one, depend on a want of oxygen. It is, probably, in this way that the normal fat is formed, when there is a full supply of oxygen, and it appears to be a species of fermentation, in which the liver seems to be somehow concerned, and hydrogen gas is given off, which of course is immediately oxidised into water in the body. Calf's liver, when placed in water, gives off hydrogen by a species of fermentation, and fat, the same as occurs in blood, is found at all times in bile. The supposed fatty fermentation of sugar actually occurs out of the body, as in the butyric fermentation, butyric acid being a true fatty acid, and being found in butter and fat, and in the fermentation of starch-sugar, where rutylic and margaric acids, of the same series, are produced, and are found, along with hydrated oxide of amyle, in the oil of grain or potato spirit.

The following table will show the derivation of fatty acids from sugar by fermentation. It will be seen that acetic acid, which, although belonging to this series, is not oily, may be formed from sugar by a polymeric transmutation, but that all the rest are obtained by the separation of carbonic acid and hydrogen, always in equal proportions. Most of the acids require so much sugar as will yield 3 eqs. of acid, and therefore we represent all as formed in that quantity; but obviously, where the number of the equivalents of sugar is divisible by 3, we may trace the formation of 1 eq. of acid.

Acids						
Name.	Formula.	Eqs. of Sugar yield.	Eqs. of Acid.	Eqs. of Carbonic Acid.	Eqs. of Hydrogen.	
Acetic	C ₂ H ₄ O ₄	1	3	0	0	
Propylic	C ₃ H ₆ O ₄	2	3	6	6	
Butyric	C ₄ H ₈ O ₄	3	3	12	12	
Valerianic	C ₅ H ₁₀ O ₄	4	3	18	18	
Caproic	C ₆ H ₁₂ O ₄	5	3	24	24	
Enanthylic	C ₇ H ₁₄ O ₄	6	3	30	30	
Caprylic	C ₈ H ₁₆ O ₄	7	3	36	36	
Pelargonic	C ₉ H ₁₈ O ₄	8	3	42	42	
Rutylic or rutic	C ₁₀ H ₂₀ O ₄	9	3	48	48	
Margaritic	C ₁₁ H ₂₂ O ₄	10	3	54	54	
Laurostearic	C ₁₂ H ₂₄ O ₄	11	3	60	60	
Cocinic	C ₁₃ H ₂₆ O ₄	12	3	66	66	
Myristic	C ₁₄ H ₂₈ O ₄	13	3	72	72	
Benic	C ₁₅ H ₃₀ O ₄	14	3	78	78	
Palmitic	C ₁₆ H ₃₂ O ₄	15	3	84	84	
Margaric	C ₁₇ H ₃₄ O ₄	16	3	90	90	
Stearic	C ₁₈ H ₃₆ O ₄	17	3	96	96	
Balenic	C ₁₉ H ₃₈ O ₄	18	3	102	102	
Arachidic	C ₂₀ H ₄₀ O ₄	19	3	108	108	
Behenic	C ₂₁ H ₄₂ O ₄	20	3	114	114	
Cerotic	C ₂₂ H ₄₄ O ₄	21	3	120	120	
Melissic	C ₂₃ H ₄₆ O ₄	22	3	126	126	

It will be seen that 1 eq. of each of the acids—butyric, cœnanthyllic, rutylic, cocinic, palmitic, and balenic acids—might be derived from 1, 2, 3, 4, 5, 6, and 9 eqs. of sugar respectively. Also, that the number of eqs. of sugar required to yield 3 eqs. of any acid is always exactly one less than half that of the eqs. of carbon in the acid. The derivation of oxide of lipyle and of oleic acid, both of which contain more carbon than hydrogen, from sugar, by fermentation, is probably not so simple as that of the volatile oily acids; but it can hardly be doubted that they may be thus formed, as they are abundant in many animal fats.

We conclude, therefore, that the origin of fat in the animal body is threefold. First, it is derived, ready formed, from plants; secondly, it is formed, in the absence of oxygen, or when oxygen is deficient, by the deoxidation of sugar, which thus supplies the oxygen wanted; and thirdly, it is also formed by a species of fermentation, along with carbonic acid and hydrogen, the latter being converted into water by the oxygen of the blood.

With reference to the tissues, fat is of great importance, as it seems to aid in the formation of cells, and it exists, accordingly, like water in a wet sponge, mechanically in the substance of most tissues, from which it may be pressed out. It has an important share in producing nervous matter; but perhaps its chief function is to aid in yielding the animal heat by its oxidation in the course of the circulation. To this we shall return hereafter.

Let us now briefly consider the process of respiration. The venous blood, loaded with the carbonic acid which it has brought from the remotest capillaries, where every change leads finally to the formation of carbonic acid, is sent to the lungs, and in the pulmonary cells exposed to the action of inspired air, separated from it by a membrane of extreme tenuity. Here the laws of diffusion of gases, in contact with an absorbent liquid, come into play. The blood gives off carbonic acid, and takes up hydrogen in its stead. The separation of the carbonic acid from the venous blood, which is absolutely essential to life, cannot take place in an atmosphere containing much carbonic acid. Hence, if the inspired air contain 10 per cent. or upwards, of carbonic acid, and only 10 per cent. of oxygen, the blood does not get rid of its carbonic acid, and death ensues. This happens when animals are forced to breathe the same air for a long time, because every respiration adds to the carbonic acid and diminishes the oxygen. Even with 1 per cent. of carbonic acid, and 19 or 20 per cent. of oxygen, oppression is felt. But if, while carbonic acid be added, oxygen be also added, the air will still admit of the diffusion of carbonic acid from the blood. It has been shown that animals can live in air containing from 17 to 23 per cent. of carbonic acid, provided it contain 35 or 40 per cent. of oxygen; so that the poisonous action of carbonic acid depends on its preventing the diffusion outwards of the carbonic acid of the blood. Hence

the importance of ventilation. The air in a crowded, ill-ventilated room, soon becomes unfit for diffusion, because, while the oxygen is diminished, the carbonic acid is increased. The expired air, with normal respiration, instead of at most $\frac{1}{1000}$ of carbonic acid, the quantity in the atmosphere, contains 3.5 to 5 per cent.; that is, from 35 to 50 times as much as the air inspired. With very deep respiration, the carbonic acid in expired air increases to 85 or 90 times that of the inspired air. The oxygen in the former case is diminished from 20 to 15 or 16½ per cent.; in the latter, to 11 or 11½ per cent. In the blood, these two changes balance each other, for it absorbs oxygen, and gives out carbonic acid nearly, but not quite, in the same volume, a part of the oxygen absorbed being converted into water. The blood has the very remarkable property of absorbing both oxygen and carbonic acid, the former by means not yet fully understood, the latter by the presence of alkaline salts, which means enable it to absorb far more of both gases than an equal bulk of water could do. Blood can absorb 13 or 14 times more oxygen than water. Whichever be the gas present in largest quantity, is readily given out in an air containing little of that gas, but is not given out in an air in which much of the gas is present. The density or rarity of air is a matter of far less consequence, than that it should contain little carbonic acid, in order to allow the venous blood to give off its carbonic acid. When it can do so, it takes up oxygen, and becomes arterial, and is then sent to the left auricle, and, entering the left ventricle, is sent to carry its oxygen to all parts, and exchange it for carbonic acid, probably produced by previous supplies of oxygen.

Verdil has recently discovered, in the parenchyma of the lungs, a peculiar acid, which he has named *pneumic acid*. The acid liquid obtained by chopping the lungs small and mixing them with distilled water, is strained, and coagulated by heat, to separate albumen. It is then neutralised with baryta water, and evaporated to $\frac{2}{3}$ of its bulk in the water bath. Sulphate of copper is now added to separate the last traces of albumen, with fatty matter, &c., and any excess of the sulphate is precipitated by a little sulphide of barium. The filtered solution is now evaporated till crystals of sulphate of soda appear, a little diluted sulphuric acid is added, and the whole is boiled with absolute alcohol, which dissolves the pneumic acid, leaving the sulphate of soda undissolved.

The new acid crystallises from alcohol in brilliant needles, forming radiate groups. At 212° it loses no water. Heated more strongly, it melts, and is decomposed. It is very soluble in water, insoluble in cold, but soluble in boiling alcohol, insoluble in ether. It forms crystalline salts with bases, and expels carbonic acid from the carbonates.

Its precise formula is not known, but it is said to contain carbon, hydrogen, nitrogen, sulphur, and oxygen.

The function of pneumatic acid is as yet unknown, but, like lactic acid, it probably exists in the blood or tissue combined with some base.

The way in which the oxygen and carbonic acid are absorbed by the blood, and yet so easily given off when wanted, may be illustrated by other chemical changes. From the change in color of the blood-corpuscles, they are probably the substance to which the oxygen is attached, when absorbed. If an engraving be exposed to the vapor or gas of iodine, the ink will take up iodine, in proportion to its thickness; and if the engraving be now pressed on paper covered with starch and moistened by an acid, a blue impression is obtained. Here the iodine leaves the ink for the starch. If the blue impression be now placed in contact with silver or copper, the iodine leaves the starch for the metal, and if the silver or copper plate be now exposed to the vapor or gas of mercury, the mercury will attach itself to the parts not acted on by the iodine, as in the daguerreotype, and produce a daguerreotype copy of the engraving without the aid of light. Now we may suppose the blood-corpuscles to take up oxygen, to yield that oxygen to the effete tissues, oxidising them, and then to take up the carbonic acid and convey it to the lungs, where it is given off by diffusion. An animal dies instantly in pure carbonic acid, because in that gas no diffusion of carbonic acid can take place; but it lives for a time in hydrogen, because in that gas the carbonic acid can leave the venous blood, and the oxygen already in the lungs can support for a time the vital process.

We see, then, that the arterial blood conveys oxygen to all parts of the system, and that this oxygen is given out by the venous blood as carbonic acid, and as water by the lungs, skin, and kidneys. This oxidation of carbon and hydrogen not only carries on the vital chemical changes, but also yields the animal heat, which is therefore produced, not in the lungs, but everywhere, chiefly in the capillaries. Now a working man consumes nearly 14 oz. of carbon, and produces about 25 cubic feet of carbonic acid in 24 hours, containing about 37 oz. of oxygen. The quantity of water produced is also ascertained, for all the oxygen is not converted into carbonic acid. And if we calculate the amount of oxygen consumed in 24 hours, and knowing how much of it becomes carbonic acid, consider the remainder as forming water; we can then deduce, from the known amount of heat given out in the conversion of so much oxygen into carbonic acid and water by combustion, the amount of heat which ought to be given out in the slow oxidation of carbon and hydrogen in the body, which is the same as in combustion, only spread over a longer period. This calculation is found to agree closely with the amount of animal heat, as directly observed, and therefore we are satisfied that the animal heat is entirely due to the chemical changes, all depending on oxidation, which go on in the

body. It is evident that the animal heat is promoted by every thing that increases the supply of oxygen, as increased respiration, or cold, which, rendering the air denser, supplies its own antidote, within certain limits, provided the food be abundant; and that clothing, which prevents loss of heat by cooling, renders a less amount of oxygen and of food necessary. Hot weather, or a hot climate, has the same effect, and reduces the appetite for food, which is the fuel to be burned in the animal furnace to produce heat. In cold climates, much more food, and especially more respiratory food, such as fat, oil, blubber, and the like, is instinctively consumed.

It is obvious also, that since carbon and hydrogen are the chief sources of animal heat in their oxidation, while nitrogen and its compounds are hardly combustible, the chief portion of the animal heat must come from the non-nitrogenous food, starch, sugar, and fat, hence called respiratory food. Indeed, so low is the combustibility of the sanguigenous food, that we may say that all the heat comes from the respiratory matter: for we find the proportion of carbon to nitrogen in the solid and liquid excreta to be as great, or greater, as in albumen, &c. Now, since the whole nitrogen is found in the excreta, it is evident that these contain also the whole carbon of the albuminous matters, or, at least, a quantity equal to it; for while the tissues contain, for every equivalent of nitrogen, 8 eqs. of carbon, urine contains, in man, only about 1·8 or 2 eqs. of carbon for 1 of nitrogen. Here 6 eqs. of carbon have disappeared for every eq. of nitrogen. But in the horse, the eqs. of carbon are to those of nitrogen in the urine as 6·6 to 1; in the cow, as 8, or even as 16 to 1; in the pig, as 10 to 1; so that in these latter cases the tissues cannot be supposed to have contributed much, if any thing, to the animal heat.

Hence the food of animals should contain a due admixture of sanguigenous and respiratory food, the former to supply the waste of the tissues, the latter to supply the animal heat. The sanguigenous food is albumen, fibrine, or caseine; the respiratory, starch, sugar, or fat. The following table, from Liebig's Letters, to which the reader is referred for full details, shows the relative proportions of sanguigenous and respiratory matter in various kinds of food, the respiratory food, for the sake of comparison, being calculated as starch.

TABLE OF THE RELATIVE PROPORTIONS OF THE SANGUIGENOUS TO THE RESPIRATORY CONSTITUENTS IN DIFFERENT KINDS OF FOOD.

	Sanguigenous.	Respiratory (as Starch).
Cow's milk contains, for	10	30 = { 8·8 fat, and 10·4 milk sugar.
Human milk	10	40
Lentils	10	21
Horse beans	10	22
Peas	10	23
Fat mutton	10	27 = 11·25 fat.

	Sanguigenous.	Respiratory (as Starch).
Fat pork contains for	10	30 = 12·5 fat.
Beef	10	17 = 7·08 "
Hare	10	2 = 0·08 "
Veal	10	1 = 0·41 "
Wheat flour	10	46
Oatmeal	10	50
Rye flour	10	57
Barley	10	57
Potatoes, white	10	86
Potatoes, blue	10	115
Rice	10	123
Buckwheat	10	130

Here we see that milk and grain, the two best forms of natural food, contain, for one of sanguigenous, 3 to 5·7 of respiratory matter. Fat meat has also 1 to 3 or 1 to 2·7, and agrees with peas and beans very nearly. Lean beef, hare, and veal, have far too little respiratory matter, only 1·7, 0·2, and 0·1, to 1 of plastic or sanguigenous food; while potatoes, rice, and buckwheat, have 8·6, 11·5, 12·3, and 13 of respiratory, for 1 of sanguigenous matter. For this reason, respiratory matter should be added to lean meat, and also to peas and beans; but sanguigenous matter should be added to potatoes and rice. This explains the instinctive and universal use of beans with bacon, pork with peas pudding (bacon containing very little sanguigenous matter), veal with ham, potatoes and rice with lean meat, flour and butter with eggs (which are very rich in albumen). The best proportion for a working man is about 5 of respiratory for 1 of albuminous food, and for a young animal, 3 or 4 of respiratory to one of sanguigenous matter. These proportions, which are those of grain and milk, are easily obtained in the mixtures above named.

When the proportion of respiratory matter is too small, then a large amount of sanguigenous matter must be used to supply heat, which is a great waste, since such matter is the worst source of heat. Thus, to obtain the same amount of heat, we must use:

Fat	100 parts; Respiratory food.
Starch	240 " " "
Cane-sugar	249 " " "
Grape-sugar	263 " " "
Spirits, at 50 per cent. of alcohol.....	266 " " "
Fresh lean meat	770; Sanguigenous food.

Alcohol belongs to the respiratory class; and, therefore, if properly diluted, and used as an addition to sanguigenous food, such as lean meat, cheese, eggs, or peas and beans, it is useful, rather than hurtful. But if added to food already containing 5, 6, 10, or 15 parts of respiratory, for 1 of sanguigenous matter, it is hurtful, as reducing the proportion of the latter still further. Now when the food contains too little sanguigenous food, enormous quantities of it are required to supply the waste of matter. Thus it will take 123 parts

of rice to supply as much tissue as 33 parts of fat pork, or 125 of blue potatoes to yield as much tissue as 27 of lean beef. But the quantity of rice or potatoes which may be used is limited by their price, and also by their bulk; for the necessary supply may be too bulky for the stomach which has to digest it, and of course a large amount of respiratory matter is wasted in the use of such food. If the peasantry attended, or were taught to attend, to the due admixture of their food, they might cause their limited wages to go much further than at present. But for details on this subject I must again refer to Liebig's *Animal Chemistry*, and to the third edition of his "*Letters on Chemistry*."

The amount of bodily or mental work done is measured by the daily waste of tissues, muscular or nervous, &c., and the daily food must contain, if health is to continue, exactly as much sanguigenous matter, and in an available form, as will supply the daily waste. With less, the body is wasted. With more, the blood is loaded with products of change beyond the normal standard, and disease ensues, if this go beyond certain limits. The respiratory food not only gives the animal heat by its oxidation, but protects against oxidation the blood and tissues. A full supply of it is equivalent to so much clothing; and *vice versa*, warm clothing enables men to do with less respiratory food.

Such is the relation of respiration to digestion and nutrition, and it will be seen that they are mutually indispensable. In digestion the food is rendered soluble, and prepared for assimilation and for oxidation. In respiration the blood is oxidised, and carries oxygen to assist in the waste of tissue everywhere, while it gives off the carbonic acid formed by previous changes.

We have now to consider the mineral elements of food, and the share they take in the vital process. All food, capable of sustaining animal life, must contain mineral salts. These are alkaline and earthy phosphates and sulphates, common salt, and oxide of iron, with, in a few cases, iodides, and in all a minute proportion of fluorides.

The blood, in order to perform its functions, must be alkaline, and it is rendered alkaline either by carbonate of soda or by phosphate of soda, PO_4 , 2NaO , H_2O , or by both. The first occurs in herbivora; the second in carnivora, and in animals fed on grain, peas, &c., alone; the third in omnivora. It is very remarkable that two salts, so different in composition as carbonate of soda, Na_2CO_3 , and phosphate of soda, 2NaO , H_2O , P_2O_5 , should yet closely agree in being alkaline, and in their action on carbonic acid in the blood. They both readily absorb it, and as readily give it out in another gas.

But while the blood, the saliva, the intestinal secretion, the bile, and milk are alkaline, and the pancreatic juice either alkaline or neutral, the juice of the muscles, the gastric juice, and the urine of carnivora and omnivora are acid. Even the urine of herbivora, al-

though permanently alkaline, is acid from excess of carbonic acid as it leaves the body. This soon evaporates, and the urine becomes alkaline from the presence of alkaline carbonates. The acidity depends, in the juice of flesh, on the presence of phosphate of potash, P O_5 , K O , 2 H O , which is an acid salt, and yet is formed in close proximity to the alkaline phosphate of soda, the blood and juice of flesh being separated only by very fine membranes. An alkaline state of the blood is absolutely indispensable to its functions; acid blood is inconsistent with life. Hence every acid that enters the blood must be at once neutralised. And yet it is in close proximity to, and communicates by endosmosis and exosmosis with, an acid liquid, the juice of flesh, or gastric juice, or urine, and is constantly receiving uric acid and other acids. Vegetable acids, taken in the food, are speedily oxidised in the blood into carbonic acid and water, and only appear as alkaline carbonates. It would appear that the formation of tissues cannot go on without the presence of free phosphoric acid, or at least acid phosphates, while their destruction demands the presence of free alkali, which we know to be favorable to oxidation. Thus, in the egg, the phosphoric acid is in great excess. As the lymph and chyle are also alkaline, the formation of the blood itself appears to depend on the presence of excess of alkali. The flesh of all animals is the same in respect to mineral matter; but the blood, and of course the urine, of the herbivora contains less phosphates and more carbonates.

The ashes of the food are either phosphates and sulphates alone, as in flesh, grain, peas, &c., or phosphates, sulphates, silicates, and carbonates, as in grass and green vegetables. They are partly soluble in water, partly insoluble. Now, in the body, the soluble parts of the ash are found in the urine, the insoluble in the solid excreta. When the phosphoric acid is not present in sufficient quantity to unite with all the bases, it forms insoluble salts with lime and magnesia, while the alkalies appear as sulphates and carbonates. But where more phosphoric acid is present, the insoluble salts are, as before, phosphates and silicates of lime, magnesia, and oxide of iron, while the soluble ones are phosphates and sulphates of the alkalies. Hence, knowing the nature of the ashes of the food, we can tell the salts of the urine and feces; and by altering the food, we can change these at pleasure. The uric and hippuric acids formed in the change of matter, are found, so far as not oxidised in the urine, and the following table shows the composition of the urine with food composed of flesh, grain, and leguminous seeds, and also with grass, clover, turnips, potatoes, and fruit. The earthy phosphates and carbonates, it must be remembered, are soluble in excess of acid.

Since the *soluble* salts of the ashes of the blood are the same as those of the urine, and since we can affect the nature of the urine by change of diet, we may not only draw conclusions as to the soluble salts of the blood from the urine, but also modify these by diet.

With food consisting of Flesh, Bread, Peas, Beans, &c., the urine contains:	With food, such as Hay, Clover, Turnips, Potatoes, Fruit, &c., the urine contains:
Free Phosphoric acid	Free Carbonic acid
Phosphates of { Lime, } dissolved by	Carbonates of { Lime, } dissolved in
{ Magnesia, } excess of acid	{ Magnesia, } excess of acid
Phosphates } of the alkalies.	Carbonates } of the alkalies.
Sulphates } of the alkalies.	Sulphates } of the alkalies.
Urates } of the alkalies.	Hippurates } of the alkalies.
Hippurates } of the alkalies.	
This urine is <i>permanently acid</i> .	This urine has a <i>transient acid</i> reaction, and a permanent alkaline one.
Acid urine usually contains uric acid.	It contains no phosphoric, and no uric acid.

When we consider the absolute necessity of phosphoric acid and the phosphates, as well as of the other mineral ingredients of food, to the vital changes, we see how important it is that the food should contain these in due proportion and admixture. This is the reason that fibrine alone will not support life; that yolk of egg, cheese, and similar matters, also fail, when used alone, to support life. The fibre of meat is rich in phosphoric acid, but has lost the alkalies of the juice: the yolk of egg is still richer in phosphoric acid, but wants the alkali of the white. Cheese is also rich in phosphoric acid, but requires the alkalies of the whey, and so on. Salt is useful, both with eggs and cheese, to supply soda for the blood and bile; indeed it is useful with all food, but still more with those substances. It appears generally to promote the secretions, probably from its adding to the solvent powers of water. Meat, boiled to rags, is fibrine, and is only nutritious with the soup. Hence the continental habit, of eating the boiled meat, after the soup made from it, is rational. All food, to be fully nutritive, must contain iron; and those kinds of animal food, which are found by experience to yield less blood, are deficient in iron as well as alkalies. Such are milk, eggs, and fish, all of which are allowed to form part of the fasting or meagre diet of Catholic countries.

The reader will find, in Liebig's "Letters on Chemistry," numerous analyses of the ashes of blood, flesh, milk, cheese, grain, fish, eggs, urine, and fæces, establishing the general principles here laid down, and the great importance of the mineral constituents. Our space is too limited to allow more than a statement of the principle, that phosphoric acid in excess is required for the production of the tissues, and excess of alkali is required to form the blood, and enable it to perform its functions of destroying the tissues by oxidation. The blood, indeed, conveys to all parts the materials for the formation of the tissues, but as that formation requires free phosphoric acid, it probably takes place out of the blood.

We have already stated that food ought to contain a due proportion of sanguigenous and respiratory matter. In preparing it, care should be taken to lose nothing of the mineral elements. Hence the salting of meat, which expels by exosmosis a great part of the juice with its salts, is injurious, unless the salts are replaced by a free use

of green vegetables, which contain much saline matter, sometimes 10, 15, or 20 per cent. of the dried plant, or by preserving the juice, boiling it down to get rid of the salt, and using it as sauce to the meat, or by adding the soluble extract of meat. The system, so common in England, of boiling food of any kind in a large quantity of water, which is thrown away, is also very bad. Vegetables ought to be stewed, with very little water, and the juice eaten with them. Meat ought either to be roasted, stewed, or if boiled for eating, boiled as follows: The meat is thrown into boiling water, and kept at 212° for a minute or two; this coagulates the albumen of the juice near the surface, so as to form a kind of crust or coat. Cold water is now added so as to reduce the temperature to 165° , at which it is kept till fully dressed in the centre. The crust of albumen keeps in the juice, and meat thus boiled is not only tender, but has all the flavor and nutritive power of roast meat. But if the soup be wanted, then the meat is put on with a little cold water, and slowly heated to boiling. The water enters and the juice is expelled; before the albumen of the latter is coagulated; and after boiling for a little, the best possible soup is obtained.

If, in countries like Australia, Buenos Ayres, and others, where cattle are killed for their hides alone, or for the hide and tallow, the flesh were thus exhausted, and the soup, using only about as much water as meat, evaporated to a soft extract, this, the true extract of meat or portable soup, would be obtained at a cheap rate, and furnish a valuable article of food, 1 part of which is equal to nearly 30 of fresh meat. This is to be carefully distinguished from the portable soup in hard gelatinous cakes, which consists chiefly of gelatine extracted, by long boiling, from meat and bones, and sometimes does not contain even $\frac{1}{10}$ th of true extract. Gelatine cannot yield blood, and is worthless as food, save perhaps in a very small proportion, to yield membrane. The true extract of meat is always soft, and does not gelatinise, and would be invaluable for convalescents and wounded soldiers. It is slightly deficient, compared with meat, in phosphoric acid, but that is easily supplied by grain or peas.

It is hardly necessary to point out the importance of salt as a chief source of sodium or soda for the blood and bile. The absence of salt is sure to be injurious, and in countries where it is scarce, it fetches a price equal to that of gold or silver. Animals instinctively take it, and search for it, and its effects on them, on their general health and all their secretions, are most marked.

Of all food, perhaps good bread, made from the whole meal of wheat, oats, or rye, is the most economical, since nature supplies in it the due proportion of sanguigenous, respiratory, and mineral matter. But since the fibrine of flour is identical with that of flesh, and fat corresponds to a certain amount of starch, fat meat agrees closely with bread, and has a better proportion of ingredients than peas, beans, and lentils. Hence the doctrine of the vegetarians is:

founded on a mistaken assumption, that there is a radical difference between meat and vegetables. It is certain that the structure of man fits him for the use, though not the exclusive use, of animal food; and even the vegetarians do not exclude milk, cheese, and eggs, all of which are of animal origin; the first about equal to meat in sanguigenous value; the two last greatly exceeding it. A man may feed as fully, nay more fully, and form more blood on a vegetable diet, one of peas, for example, than on one of very fat meat. There is no known difference in the power of forming blood, between flesh and bread, if the flesh be mixed with sufficient fat or some starch; and there is one reason why flesh should form part of man's food, besides that derived from the structure of his teeth and digestive organs, namely, that since the chief use of food is to supply the waste of muscle, the best substance for this must be the muscle of animals. The great error in diet is not that of eating flesh, but of eating too much flesh, or too much sanguigenous matter, whether animal or vegetable. And the only true principle of diet is to obtain the necessary amount of sanguigenous matter, of respiratory matter, and of mineral salts, no matter from what sources. In applying this rule to man, a mixed animal and vegetable diet is obviously the best; both as being in the end most economical, because flesh is nearest of all to what it has to supply; and because, although fat can replace the starch of vegetables as a source of heat, the ashes of vegetables yield a more abundant supply of alkalies. The instinct of man agrees entirely with this view, and, like all one-sided and exclusive ideas, vegetarianism is inconsistent with nature. Still, it is certain that men can over-eat themselves more easily with animal than with vegetable food, and that they can live on vegetables alone. But they are not intended, by their structure, to do so, and even on vegetables may easily live too high, especially if milk, cheese, and eggs be added.

The abuse of fermented liquors is hurtful in two ways; first, by the peculiar stimulus which alcohol, unless much diluted, exerts on the nervous system in some way unknown; and secondly, by increasing the proportion of respiratory matter to sanguigenous, far beyond the proper standard. By virtue of its strong attraction for oxygen, alcohol is first oxidised, while the food and tissues are imperfectly oxidised, and disease is thus induced. If the food already contain a full or large proportion of starch or fat, every drop of alcohol is hurtful; but when the food is too rich in sanguigenous matter, wine and beer are wholesome. In proof of the fact that alcohol supplements the other respiratory food, it is observed that those who drink no wine consume far more bread, vegetables, rice, or puddings, than wine-drinkers; and the good health enjoyed by the natives of wine and beer countries, who use these liquors freely but not to excess, proves that alcohol is not essentially hurtful, when properly diluted, but acts as respiratory food. Those who

take much fat, butter, or oil, cannot take wine, and feel no desire for it. If we wish to fatten an animal, its food ought to contain a large proportion of respiratory food, the excess of which, beyond what is required for the animal heat, is converted into fat, and stored up in cells. But as sanguigenous matter is required for the change of the tissues and also to form the fat cells, an animal cannot be fattened, nor even live, on starch alone.

We have now seen that the food is digested, enters the circulation, restores the wasted tissues, and supplies during its oxidation the secretions, the excretions, and the animal heat. It is, in other words, burned in the body, as in the furnace. The products of the complete combustion of the respiratory food, namely, carbonic acid, water, and ammonia, escape by the lungs and kidneys. The products of incomplete combustion chiefly derived from sanguigenous food, are partly found in the bile, partly in the urine and feces, where they represent the soot of the furnace, and in fact are, to a great extent, identical with some of the compounds found in tar, which is liquid soot. Carboic acid, for example, is found both in urine and in tar; and urine also contains another acid, homologous with carboic acid. The ashes are divided by water into the soluble, which appear in the urine, and the insoluble, which are found in the feces, along with indigestible woody fibre, undigested starch, fetid products, which can be imitated by the partial oxidation of albuminous matter out of the body; and, lastly, tarry products, originating in the same way. The ashes of the liquid and solid excreta are identical with those of the food, if that be uniform, but change with the diet.

So long as the vital force prevails, the oxidation in the body affects only the respiratory food and the effete or worn-out tissues. It produces, however, as it advances, products which no longer obey the vital force, and, yielding to physical forces, crystallise. And these, such as hippuric acid, creatine, inosinic acid, and urea, are destined to be excreted. After death, the oxygen of the air, no longer opposed by the vital force, attacks the blood and tissues. The first effect is a degree of decay, and by contact of the decaying albuminous matter, now a ferment, with the entire albuminous compounds remaining, these putrefy, and are finally, by the process of decay and putrefaction, resolved into the organic food of plants, carbonic acid, water, ammonia, and sulphuric acid, while the ashes are restored to the soil.

Now the circuit begins again, which we have already traced. The plant grows, and from carbonic acid, water, ammonia, sulphuric acid, and the mineral salts, forms its tissues and products, ready to become the food of a new generation of animals, which at death are again resolved into food for plants. And thus the balance is kept between the animal and vegetable kingdom, the atmosphere, water, and soil, or mineral kingdom, supplying the field of contest, and the necessary media.

Although, as we have seen, animals can form blood and tissues either from albumen, fibrine, or caseine, provided the necessary salts be present, and therefore can convert those compounds into one another, there is no evidence that they can form either albumen, fibrine, or caseine, as the plant does, from any substance not containing one of them. On the contrary, the processes of animal life, being processes of oxidation and destruction, are opposed to those of vegetation. The chief vegetable products formed by animals are fat, benzoic acid, which is found in the urine of herbivora, and oxalic acid. Starch has lately been detected in various parts of the body, but its origin is still doubtful. Glucose appears to be a normal constituent of the blood in some parts, and is probably formed in the body; there is reason to believe that it is produced by the decomposition of albuminous matter. But all of these may be formed by oxidation or by fermentation. Plants are characterised chemically by construction of complex molecules and deoxidation, animals by destruction of complex molecules and oxidation, and the products of each form of life are the food of the other.

The food of carnivora, being identical with their blood and muscle, the digestive apparatus is in them very simple; and the *faeces*, consisting chiefly of insoluble phosphates, much less bulky than in herbivora. The respiratory part of their food is fat, present even in lean flesh. But as it is often deficient in quantity, they are compelled to burn a portion of sanguigenous matter for heat, a wasteful expenditure of force. This is done by muscular motion, which rapidly wastes the tissues. Hence the restlessness and constant activity of carnivorous animals, even in confinement.

The remarkable fact already noticed, of the existence in all parts of the body of an alkaline liquid, the blood, and an acid liquid, the juice of flesh, separated by a very thin membrane, and in contact with muscles and nerve, seems to have some relation to the fact now established of the existence of electric currents in the body, and particularly to those which occur when muscles contract. The animal body may be regarded as a galvanic engine for the production of mechanical force. This force is derived from the food, and with the food has been derived, as we have seen, from the solar rays. A working man, it has been calculated, produces in 24 hours an amount of heating or thermal effect equal to raising nearly 14 millions of lbs. to the height of 1 foot, heat being one form of mechanical effect. But, from causes connected with the range of temperature, he can only produce, in the form of actual work done, about as much mechanical effect as would raise 3,600,000 lbs. to the height of 1 foot, and that in 24 hours. Even this is a prodigious amount of force, and whether we regard it as derived from heat, electricity, or chemical action, it is ultimately derived from the luminous solar rays, on which vegetation depends.

Our space will not permit us to enter into detail on the chemical

nature of the causes of disease, which are still very imperfectly understood. But some things are evident. Thus, if the digestion be so far impaired, by any cause, as not to dissolve the necessary amount of respiratory matter, the tissues, no longer protected, are wasted by oxidation, and the products of this, such as uric acid, load the urine, as is seen in all febrile diseases. If this state continues, the lungs, where oxygen is absorbed, become affected. When oxygen is deficient, combustible matter accumulates in the blood beyond the due proportion, and the liver is called on to work beyond its powers, in secreting bile or forming fat, and hepatic disease ensues, as we see in hot climates, when people indulge in full feeding, and respiration is languid. Should the food be too abundant and too rich in sanguigenous matter, this amounts to a deficiency of oxygen; and if, at the same time, there be a deficiency of alkali, necessary to promote the oxidation of effete matter in the blood, we have the uric acid diathesis, or with a little more oxygen, the oxalic acid diathesis. Gelatinous food, which cannot form blood, and is deficient in alkali, and strong wines which contain no tartar, greatly promote this diathesis; light wines, which contain tartar, vegetables which are rich in alkali, exercise in the open air, and moderation in sanguigenous diet, are the best remedies. On the Rhine, where light wines are freely used, uric acid calculus is unknown as a native disease, but with drinkers of port and sherry, this calculus, as well as its concomitant gout, are very frequent. A change of diet and mode of life, on the principles we have endeavored to explain, will alter entirely the character of the urine, and of course of the blood. Hence the supreme value of diet and regimen as means of cure, acknowledged by all experienced physicians. It is probably in this direction, in the study of the secretions, and the means of changing their nature, that we may hope for the greatest practical improvement in medicine.

One question is still very obscure, namely, how that portion of insoluble phosphate which is derived from the effete tissues reaches the intestinal canal. The earthy phosphates are insoluble in water and alkaline solutions; hence they are insoluble in the blood. But yet they are conveyed, probably in some form of combination soluble in water, to the intestines. They are soluble in excess of phosphoric or carbonic acid; but the blood is never acid. But as the soluble forms of sanguigenous matter contain earthy phosphates, so it is possible that when such matter is destroyed, some of the products contain these phosphates in a soluble form. Such products, however, are still unknown. Morbid ossification probably depends on the absence or deficiency of such products; and *mollities ossium*, in all probability, is caused by a morbid excess of phosphoric acid in some part. In chlorosis, the number of red blood globules is diminished, and as these contain much iron, the disease is connected with a defect in the quantity of iron in the food, or perhaps with a

want of its proper solvent. This explains the benefit derived from the use of iron, under which the red globules rapidly increase in number in many cases. In all acute febrile diseases, and in all chronic diseases, which affect the digestive or nutritive powers, emaciation occurs, because the oxygen of the air, no longer opposed, burns off the tissues and wastes them. This explains the good effects of cod-liver oil, and other oily matters, such as olive-oil, butter, and cream, in many chronic wasting diseases: it protects the tissues till the disease has run its course, if curable, and retards the fatal termination when the disease is incurable; provided the stomach have still the power of taking up the oil. The absence of salt deranges the whole vital process, and particularly the secretion of bile, which requires soda, that is, oxide of sodium. But salt certainly acts as salt, and has, for example, a wonderful power of combining with other substances, such as sugar and urea, with both of which it forms soluble crystalline compounds. It is hardly necessary to mention that, if alcali, instead of free acid, should prevail in the urine—for healthy urine is always acid—the earthy phosphates are thrown down, and give rise to phosphatic calculus.

When children are injudiciously fed on diet composed chiefly of starch, such as sago, arrow-root, and the like, there occurs a great deficiency of blood and of bone-forming matter; fat accumulates, but the frame is weak and rickety, from small muscles and soft bones. Children ought to have a full supply of sanguigenous food, and even bread contains too little for them; milk or flesh should be added. But whether fed on bread and milk, or meat and bread, there is apt to occur a deficiency of phosphate of lime, from the rapid formation of bone. But as meat, eggs, and milk, contain an excess of phosphoric, that is, not enough of lime to convert the whole acid into phosphate of lime, $\text{P O}_5, 3 \text{ Ca O}$, lime is a good addition to the food of young children. It may be given in the form of lime-water, which the peasants of Germany give to their children with the best results, while the children, guided by instinct, greedily take it.

Since the products of the waste of tissues are sent out of the body by the lungs, the skin, the kidneys, and the intestines, we can see how the occurrence of an impediment, in any of these quarters, calls into increased action the others. Checked perspiration causes an accumulation of effete matter in the urine, which becomes loaded with products of imperfect oxidation. When, from any cause, such a check to perspiration, or to the due action of the lungs, this loading of the urine goes very far, it begins to deposit a sediment, even in the bladder or kidneys. As Prout pointed out, the effect of a purgative in this case, is greatly to increase the action of the intestines, and thus to relieve the blood and the urine, the latter acquiring its natural color, and normal composition.

The use of tea, coffee, and chocolate has become, in some form,

to all nations, as a necessary of life. Coffee, tea, and Guarana and Paraguay tea, used for the same purposes, all contain caffeine; while chocolate or cocoa contains theobromine, a body closely allied to caffeine. It would therefore appear that caffeine has a decided action on the system, promoting, in some way, the natural vital changes. Under caffeine, we have seen the very curious relation existing between caffeine and its derivatives, and uric acid and its derivatives. Besides this, caffeine closely approaches, in composition, to creatine and glycocine. We may, therefore, conjecture that it aids the change going on in some parts; that it gives a sense of refreshment and new vigor is certain, but we cannot yet trace its action, although it may very possibly promote the secretion of bile. One thing is remarkable, that no people, after once learning to use tea or coffee, ever give it up; and that the chief effects of tea, coffee, and chocolate are the same, and that tea and coffee contain the same base, and chocolate an allied one. They also are rich in mineral salts.

On all of the subjects which have been here so briefly touched upon in connection with the growth and nutrition of plants and animals, much more might be said, whether in reference to physiology, to agriculture, or to medicine. But this would be out of place in an elementary work, and the reader who wishes for more detailed information will find it in the works of Liebig, especially in the last edition of his "Agricultural Chemistry," and of his "Letters on Chemistry," and in a condensed form, in a small work which he has lately published, under the title of "Principles of Agricultural Chemistry." These works are rich in sagacious and comprehensive views on the most interesting questions. But the reader must remember, that all such views, as well as those indicated in the present work, are not to be regarded as ascertained truth, but are only the best conclusions we can draw, in the present state of our knowledge, from the best-ascertained facts in our possession. They must infallibly be modified, and in some cases, perhaps, refuted, by increasing knowledge; but in that case they will be replaced by others corresponding to the state of knowledge at the time.

SUPPLEMENT.

No department of science has made such rapid progress as that of Organic Chemistry, within the last few years. Since the last edition of this work, there has accumulated a vast number of facts, especially through the labors of the European chemists. Many of these have contributed greatly to advance the true theory of the manner in which the molecules of organic compounds are combined. But so rapidly have these discoveries accumulated upon us, that it is almost impossible to give them a methodical arrangement. This is conspicuously true in the laborious work of Gmelin, just issuing from the English press, and even in the latest edition of Gregory, from which this edition is derived.

In this supplement we shall not attempt any methodical arrangement of the new matter we introduce, for the time has not yet arrived when the great mass of valuable discoveries being made daily, are susceptible of being placed in that methodical arrangement necessary to a complete treatise upon Chemistry. Although the late discoveries of the English and German philosophers are greatly facilitating this desideratum, still many years will yet have to intervene, and very many new discoveries have to be effected, before we shall arrive at that stage of progress which will justify us in the task of giving to Organic Chemistry that true arrangement so necessary to its thorough comprehension.

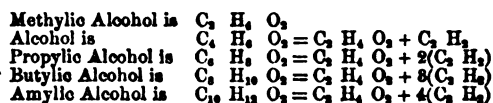
In the front of the book the reader will find a table of homologues. As these series are of the utmost importance, and as they may, in the progress of the science, prove still more so, it is necessary that the student should comprehend what is meant by homologous series of organic compounds. The following remarks by Gregory present the subject clearly :

We have already had occasion to speak of certain remarkable series of compounds, such as that of the volatile oily acids. The recent progress of Organic Chemistry has shown that such series frequently occur; nay, Gerhardt has founded on them his arrangement of organic compounds. But although it is more than probable that all may one day admit of being thus classified, at present little or nothing would be gained by adopting that arrangement,

which cannot yet be carried out. Yet the properties of such groups or series as are obviously homologous are so strikingly analogous, that it is necessary for the student of Organic Chemistry to be acquainted with those which are best known.

A series of compounds is called homologous, when each member of the series differs from the others, either by a certain number of equivalents of carbon and hydrogen, or by a multiple of it, and when the properties of these different compounds, although entirely analogous, differ in degree, and that in proportion to the amount of carbon and hydrogen.

To take an example, pyroxilic spirit, alcohol, and oil of potato spirit are three bodies belonging to an homologous series. They are homologous to each other. Let us examine their formulæ.



In this table it is seen that methylic alcohol and alcohol differ by $\text{C}_2 \text{ H}_4$; and that, at each step higher in the scale, $\text{C}_2 \text{ H}_4$ is added, so that methylic and amylic alcohols differ by $\text{C}_8 \text{ H}_{16} = 4$ times $\text{C}_2 \text{ H}_4$. The third and fourth compounds, propylic and butylic alcohols, have only very recently been discovered, but their existence had long been predicted.

Now, every known member of this series has analogous properties: they are neutral, volatile bodies, liquid in the lower part of the scale, above given, but solid and fusible in the higher parts where the carbon and hydrogen are in larger proportion. They are, in short, alcohols. They all yield ethers, bearing the same relation to the respective alcohols as ether does to alcohol. They all, when oxidised, yield volatile acids, bearing to the respective alcohols the same relation as formic acid to pyroxilic spirit, acetic acid to alcohol, and valerianic acid to oil of potato. In these alcohols, the boiling-point rises a certain number of degrees, about 34° F. , for each $\text{C}_2 \text{ H}_4$ added. The melting-point of these alcohols rises at each step in the series; but the precise amount of this rise has not yet been ascertained. The fact is well seen in these members of the series which, from being high in it, are solid at ordinary or at low temperatures. Common alcohol is not yet known in the solid state, but has been reduced to a thick, oily state by a very intense cold. The density of the vapors of these alcohols also varies according to a fixed law, rising as the amount of $\text{C}_2 \text{ H}_4$, which is added at each step, increases. The density of the vapors varies also according to a fixed law. It will be observed that the ethers and the volatile acids, derived from these alcohols, form also homologous series, differing from each other by $\text{C}_2 \text{ H}_4$, or by multiples of $\text{C}_2 \text{ H}_4$. And every derivative of pyroxilic spirit, which is the beginning or start-

ing-point of a parallel series, in which the composition varies as in the first; while the properties, analogous in each series, yet vary in each in degree, according to a fixed law, as the amount of $C, H,$ increases or diminishes. When an homologous series is once ascertained in a few of its members, the ultimate discovery of the rest may be safely predicted. In the series of alcohols, few are yet known; besides the five above mentioned, not more than five or six others, much higher in the scale, some of which are of very recent discovery. The same is true of the ethers. A few years ago, only two of the acids of the series derived from alcohols by oxidation were recognised, namely, formic and acetic acids. But that series of acids is now complete up to 40 eqs. of carbon, inclusive; and three are known beyond that point, the highest in the scale yet discovered, containing 60 eqs. of carbon. It will be observed that the few homologous series above alluded to, have been discovered simply by the analysis of the substances, and are therefore expressions of fact. It is certain that the alcohols, the ethers, and the acids of these different series differ, in each series, by $C, H,$, or multiples of it; and that in each series the properties of all the members are analogous, yet differ in degree. We cannot doubt, therefore, that the difference in properties, so regular and graduated in each homologous series, depends on the equally regular and graduated addition of $C, H,$ to the preceding molecule.

Now, if we arrange in a horizontal line, the lowest members of the different series—of the alcohol series, for example, the ether series, or the acid series—we have only to add, under each, in a descending vertical column, $C, H,$ at each step, to obtain the composition of the whole possible members of each series up to 40, 50, 60, or 100 eqs. of carbon. And the principle of such a table is so simple, that any one who has the first horizontal line can fill it up at once.

If we take the case of alcohols, we have seen that ethers and volatile acids are derived from them. But there are many more derivations, each of which finds its place in the horizontal line, and is the beginning of a vertical or homologous series. Of course, the compounds in any horizontal column, being derived from one, such as alcohol, are not analogous to each other, but totally different in properties. But the whole members of any vertical series, in our supposed table, are so analogous as to be included under the same name, and under one general formula.

Now alcohol is not the true, theoretical foundation of the horizontal series derived from it, nor is ether, but rather the supposed radical of both, in this instance ethyle, and in the case of pyroxilic spirit, which is lowest in the scale, methyle.

The first or fundamental horizontal column will contain, therefore, methyle and its derivatives; the next, ethyle and its derivatives; standing immediately under the former, with which they

are, in each vertical column, homologous. It is evident that the number of vertical or homologous series depends on that of the derivatives in the first horizontal one.

Now the derivatives of methyle are very numerous, and each is the starting-point of a series of homologous compounds. In the table, here appended, we have selected a few of the most important, extending to seventeen members or derivatives in the horizontal line, and consequently seventeen homologous series in the vertical columns.

At the head of each vertical column we have placed the general formula under which its members are included. These general formulæ would alone suffice to enable any one to construct the whole table.

In these general formulæ, n is used to signify any given number of equivalents, and in this table, as well as generally, it stands for an even number, such as 2, 4, 6, 8, 10, &c. If the number of equivalents of hydrogen exceed that of those of carbon by 1, then we write $C_n H_{n+1}$, if it fall short by 1, we write $C_n H_{n-1}$, and so on. If we wish to deduce, from the general formula, that of any particular compound, we require only to know how many equivalents of carbon that compound contains. Thus the general formula for the alcohols of this series is $C_n H_{n+1} O$, HO or $C_n H_{n+1} O_2$. What is the special formula of amylic alcohol? This alcohol yields, when oxidised, valerianic acid, in which there are 10 eqs. of carbon. Now the number of eqs. of carbon is always the same in an alcohol and in the acid which it yields; we have therefore 10 eqs. of carbon. But if, in this case, $n = 10$, $n + 1$ must be $= 11$, and the formula for amylic alcohol becomes $C_{10} H_{11} O$, HO, or $C_{10} H_{11} O_2$.

In like manner, if we could obtain margaric alcohol, we know, since margaric acid contains 34 eqs. of carbon, that the formula of margaric alcohol must be $C_{34} H_{35} O$, HO, or $C_{34} H_{35} O_2$.

Column 1. General formula, $C_n H_n + 1$. This formula represents the radicals of the methyle and ethyle series. Of these, five or six have been obtained, by Frankland and by Kolbe, in the separate form, and the names of these are given in the table.

Column 2. General formula, $C_n H_n + 1, H$, or $C_n H_n + 1$. This series is homologous with marsh gas, the hyduret of methyle, $C_2 H_2$, H or $C_4 H_4$.

Those lowest in the series are permanent gases, those above them highly volatile liquids; those still higher oily liquids, and higher still they are fatty and waxy fusible solids. This is true also of the radicals in the preceding paragraph. It is probable that one of the bodies described as paraffine, as well as some paraffine oils, belong to this series of hydurets.

Column 3. General formula, $C_n H_n + 1, O$. This represents the oxides of the preceding radicals, or ethers, of which ether is the type. A few only of these are known in a separate form, and a few

more in combination. With acids, especially organic acids, they yield compound ethers, such as oxalic or benzoic ether. Those containing much carbon are solid.

Column 4. $C_n H_n + 1, O + HO$, the hydrated oxides of the radicals, or alcohols, of which alcohol is the type. Like the ethers, they are volatile liquids in the first part of the scale, the boiling-point of which rises with the amount of carbon, and fusible and volatile solids when the carbon exceeds a certain amount; the melting and boiling points of which, and the density of their vapors, vary according to the same law, rising a certain number of degrees for each addition of $C_2 H_2$. The rise in the boiling-point is about $19^\circ C.$, or $34^\circ F.$, for each addition of $C_2 H_2$.

Column 5. $C_n H_n - 1$, the derived radicals, formed from those of the ethyle series by oxidation or dehydrogenation, of which acetylene is the type. They are, as yet, only known in combination. We therefore pass on to

Column 6. General formula, $C_n H_n - 1, H$ or $(C_n H_n)_2$. This series of hydurets is homologous with methylene, $C_2 H_2$, H or $C_2 H_2$, and ethylene or olefiant gas, $C_2 H_4$, H , or $C_2 H_4$. The former is the hyduret of formyle, the latter the hyduret of acetylene.

These compounds much resemble those of column 2, but differ from them in being more readily acted on by chlorine, even in the dark. They are, like the others, gases when low in the scale; then, as we rise in the series, highly volatile liquids, less volatile and oily liquids, fatty and finally waxy solids. Various forms of paraffine and of paraffine oil belong to this series.

Column 7. $C_n H_n - 1, O + HO$, the aldehydes, or hydrated oxides of the immediately preceding radicals, of which aldehyde is the type. Several are known, and they are characterised by reducing the salts of silver, so as to yield a mirror-like deposit of metal; while they pass, by oxidation, into volatile acids, which are the hydrated teroxides of the same radicals, as aldehyde does into acetic acid. It has recently been shown, by Bertagnini and others, that the aldehydes form crystallisable compounds with bisulphite of potash, soda, or ammonia. By this means we can detect the presence of aldehydes in mixtures, and even purify them from other volatile liquids.

Column 8. $C_n H_n - 1, O_2, HO$, or $(C_n H_n)_2 O_2$. These are the volatile acids already alluded to, and yield the most complete series of homologous compounds yet known. They are almost all found in nature, and all but the two first are oily or fatty acids, the boiling-point of which rises about $19^\circ C.$, or $34^\circ F.$, for every step in the scale. The most abundant and important fatty acids, such as stearic and margaric acids, cocinic and palmitic acids, and the acids of wax, belong to this series.

Column 9. $C_n H_n - 1, O_2, NH_4 O$, the compounds of the prece-

ding acids with ammonia. These are here introduced, because, when deprived of 4 eqs. of water, they yield the next series.

Columns 10 and 11. $C_n H_n - 1, N$, or $CH_n + 1, C_n N$. The first of these formulæ, which are isomeric, namely, column 10, represents what are called *nitryles*, that is, compounds of nitrogen with the radical of the acid of the ammonia salt, from which the nitryle is derived. Thus acetate of ammonia, deprived of 4 eqs. of water, that is, of all its oxygen, and 4 eqs. of hydrogen, yields acetoni-
tryle,



The second general formula, column 11, represents the cyanide, not of the radical of the acid from which it has been formed, but of the original radical of the ethyle series, one step lower in the scale than the acid. Such a cyanide must be isomeric with the nitryle of the acid radical. For acetoni-
tryle, $C_4 H_7 N$, is the same, empirically, as the cyanide of methyle, $C_2 H_5 + C_2 N$.

In point of fact, some of the nitryles really are such cyanides, and it is possible that all may prove to be so. But it is also possible that both compounds may exist, and therefore we have given both formulæ.

Column 12. $C_n H_n - 1, O_2 + C_n H_n + 1, O$, or $C_n H_n O_4$, the compound ethers formed by the combination of one of the volatile acids with the ether from which it is derived; of these, acetate of oxide of ethyle, or acetic ether, is the type. If we represent them by the general formula, $C_n H_n O_4$, the amount of C and H is always exactly double of that in the hydrated acid itself. Acetic acid is $C_4 H_8 O_6$, and acetic ether is $C_6 H_{12} O_4$. Many of this series are known and occur in nature. It must be observed that each ether can combine not only with the acid related to it, which has the same number of eqs. of carbon, as, oxide of ethyle with acetic acid; oxide of amylic with valerianic acid, &c.; but also each ether can combine with all the acids, and each acid with all the ethers of the two series. It is only, however, when the acid and ether which combine have the same number of eqs. of carbon that the relations above pointed out hold good. Thus, acetic acid combines with amylic ether, and gives the compound $C_{10} H_{18} O, C_4 H_8 O_2 = C_{14} H_{14} O_4$, which still comes under the general formula, but in which the carbon and hydrogen are not double of those in the acid or ether, as in the case of acetic ether above given. The compound of acetic acid with amylic ether just named occurs in nature, and can be made artificially. It gives the peculiar and agreeable flavor to the pear, while acetic ether contributes in part to that of the pineapple, along with another compound of the same class, butyric ether, that is, butyric acid combined with oxide of ethyle, $C_4 H_8 O, C_4 H_8 O_2 = C_{12} H_{18} O_4$.

Column 13. $C_n H_n + 1, Cl$, the chlorides of the radicals of the

ethylic series. Chloride of ethyle is the type. Of course similar series exist for the bromides and iodides. Several of them are known, and have been used with advantage in recent researches.

Column 14. $C_2 H_2 + \text{, S}$. The sulphides of the same radicals. These are volatile fetid liquids, so far as known.

Column 15. $C_2 H_2 + \text{, S, HS}$. The preceding, combined with sulphuretted hydrogen, or, as they may be called, mercaptans. The type is mercaptan, of the ethylic series, $C_2 H_2 S$, HS. These also are horribly fetid. Only a few are known as yet.

Columns 16 and 17. $C_2 H_2 + \text{, N H}_2$, the amides of the radicals of the ethylic series, which are isomeric, if not identical, with a very remarkable series of bases, already alluded to as derived from ammonia by the replacement of 1 eq. of its hydrogen by 1 eq. of one of these radicals. The last column, 17, contains the empirical formula of these bases, $C_2 H_2 + \text{, N}$. Methylamine, $C_1 H_3 N$, or ethylamine, or $C_2 H_5 N$, is the type. Already six or seven of these bases are known.

More columns might be added, almost *ad infinitum*, as for example, the bisulphates of the oxides of the ethylic radicals, which act as acids, and of which sulphovinic acid is the type. But the above will suffice to explain the doctrine of homologous compounds. It will be seen that when we know the formula of a compound, belonging to this series, we can predict its general characters, physical and chemical. The former depend on its place in the vertical column to which it belongs, the latter on the general formula appropriate to that column. For example, if I analyse a substance, and find its formula to be $C_{10} H_{18} O_2$, or $C_{10} H_{17} O$, HO, I observe that it belongs to the general formula $C_n H_{2n} + \text{, O, HO}$, that of the alcohols. If it be $C_{20} H_{40} O_2$, or $C_{20} H_{39} O$, HO, it belongs to the aldehydes, $C_n H_{2n} O_2$; if $C_2 H_2 N$, it belongs to the bases, in column 15, and in each case I know what its chemical characters will be. But the first, although an alcohol, will be less volatile than common alcohol; the second far less volatile than aldehyde, perhaps a solid at the ordinary temperature; and the third, although a base, analogous to ammonia, will be a liquid at ordinary temperature, less volatile than methylamine and ethylamine, which indeed are gases at ordinary temperatures, but easily condensed.

If the body analysed be of the formula $C_n H_{2n} O_n$, it must be either acid or neutral. If acid, it will be volatile and oily, or fatty, provided it contain six or more eqs. of carbon. If neutral, it will be a compound ether, see column 12, containing a volatile acid, united to an oxide of one of the radicals in column 1.

It is more than probable, that every organic compound belongs to an homologous (or vertical) series, if we could only ascertain the other members of it. And it can hardly be doubted that series will be discovered, in which the common difference or addition at each step is not $C_1 H_2$, but some other group. Yet $C_1 H_2$ appears to be the

commonest, for there is another series, or rather set of homologous series, quite distinct from that here explained, in which the starting-points are very different, but the common difference is still C, H_2 . In this there is an acid series, of which the starting-point is benzoic acid, $C_6H_5O_2$, and a basic series, of which the starting-point is aniline, C_6H_5N ; besides various other series, all of which may be included under the name of the benzoic series (just as the table above given may be called the ethylic series), in which C, H_2 is also added at each step.

It will not escape the reader, that the foundation of the ethylic series is laid in inorganic chemistry. Thus methyle, C, H_2 , the first radical, if C, H_2 be taken from it, yields H , that is, hydrogen; its ether and its alcohol, minus C, H_2 , alike yield HO , or water. Its acid, formic acid, C, H_2O_2 , yields O , oxygen. Formonitryle, C, HN , is hydrocyanic acid, or cyanide of hydrogen; chloride of methyle, C, H_2Cl , minus C, H_2 , is hydrochloric acid; sulphide of methyle, minus C, H_2 , is sulphuretted hydrogen; and lastly, methylamine, C, H_5N , minus C, H_2 , is ammonia, the very type of the methylamine series of bases. Indeed, it is not easy, without analysis, to distinguish methylamine from ammonia.

Hydrogen, then, is the true starting-point of the ethylic series of radicals, and ammonia of the ethylic series of volatile bases.

Such is the doctrine as exemplified in one well-marked instance of homologous compounds, a doctrine which has already done much, and is destined to do much more, in simplifying our knowledge, and enabling us to classify the immediate facts of organic chemistry.

At the meeting of the British Association in Ipswich, M. Dumas drew the attention of the Association to the extraordinary analogy between homologous groups of organic compounds and certain small groups of elementary bodies, which have long been observed. The best example is that of chlorine, bromine, and iodine, which differ from each other precisely as do three contiguous homologous compounds in the table; that is, in properties. Thus chlorine is an easily condensable gas, bromine a volatile liquid, iodine a volatile solid. In affinity, bromine is intermediate between chlorine and iodine, as it is in atomic weight. This is obviously true also of the organic group, say, for example, of methyle, ethyle, and propyle, or of formic, acetic, and propylic acids, or of methylamine, ethylamine, and propylamine. M. Dumas is said by some journals to have drawn the conclusion that, since the equivalent of bromine is the mean between those of chlorine and iodine, therefore bromine is made up of half an equivalent of chlorine and half an equivalent of iodine. But it is probable that he only indicated the possibility of this.

Now, although M. Dumas may have been the first to point out strongly in public the remarkable analogy between the elementary groups, chlorine, bromine, iodine, potassium, sodium, lithium, &c.,

&c., and homologous organic groups, such as methylamine, ethylamine, and propylamine, yet it must not be supposed that this had escaped the notice of chemists. The author of the present work has for several years pointed it out in his lectures; nay, before the homologous organic groups were known, the late Dr. Turner and other teachers, including the author, constantly drew attention to the analogy between chlorine, bromine, and iodine, as furnishing an argument for their being truly compound. But they took a different view from that of M. Dumas, and one still more analogous to what is known of homologous bodies; namely, that chlorine, bromine, and iodine had the same base or substratum, with a different addition in each case. And since the discovery of homologous bodies, it has been regarded as highly probable by the author, and mentioned as such in his lectures, that there is here also a common difference, corresponding to C, H_2 in the ethylic series, the addition of which, in increasing quantity, converts chlorine into bromine, and bromine into iodine. It is evidently unnecessary to suppose any difference in the quality of what is added, because we see, in the organic compounds, that a difference in its quantity is amply sufficient to alter the density, the fusing and boiling points, &c., &c.

This has been explained fully, because M. Dumas has been said to have founded on these facts and hypotheses, an opinion that we may hope, on the principle laid down by him, to transmute one element into another. Thus we may hope to fuse one atom of chlorine and one atom of iodine into two atoms of bromine, &c. And of course, if we could discover any metal homologous with gold, as sodium is with potassium and lithium, we might expect to convert that metal into gold.

The idea on which recent attempts at transmutation have been founded, is different. It is derived from the remarkable changes produced in both simple and compound bodies by a new arrangement or grouping of the ultimate atoms into molecules of various size. Charcoal, graphite, and diamond, are all carbon, yet how different! The two last crystallise in forms geometrically distinct. So does sulphur, which also exists in a third or amorphous state. Phosphorus is at one time a white, translucent, fusible, and easily combustible body; at another, a red substance, not easily fusible, and hardly combustible, save at a red heat, when it passes into the first state. And compounds, although of the same composition in 100 parts, may vary *ad infinitum* in character. Hence it was supposed that, by a new arrangement of the same atoms, a different, even although elementary substance, might be obtained; and Dr. Brown stated that he had thus converted carbon into silicon. Supposing this to be confirmed, it is easy to imagine lead or iron converted into gold. Even charcoal and diamond, although chemically identical, are physically far more different than are lead and gold, and, in short, transmutation was clearly conceivable.

But, although this be the case, yet we must not forget that, until Dr. Brown's experiments be confirmed, the most widely differing forms of elementary bodies—of carbon, for example—all agree in some essential chemical properties; for example, in yielding carbonic acid when burned in oxygen gas. Whereas carbon and silicon, even in the alleged results of Dr. Brown, cannot be made to yield the same products. We have no proof, as yet, that the same atoms, differently grouped, can yield a body which has entirely new and permanent chemical properties. This is conceivable, and, strictly speaking, possible; but we have, as yet, no proof of it. And the same is true of M. Dumas's suggestion; it is conceivable, but we have no proof that it can be done with truly elementary bodies, or even with such as are elements to us.

It is, we conceive, much more probable, that chlorine, bromine, and iodine, are really homologous *compounds*, and not elements; and if we can discover their common difference (their C, H_2 , so to speak), we may hope to transmute them into each other. And so of all other similar groups.

But, admitting the possibility of a transmutation, it must not be forgotten that it is almost an absurdity to suppose it easy or practicable under ordinary circumstances, or that it should ever become so. It must require some very great and unusual force; for if it were otherwise, if one element could easily pass into another, external nature must come to an end. Nay, if carbon could readily become silicon, how could our bodies or the vegetable world exist? In them, nearly two-thirds of the weight is carbon; and if that were changed, even in part, to silicon, or to any other element, what must be the result?

It has always appeared to us, that those bodies which are best known, and which resist most powerfully all our efforts to decompose or transmute them, must have, in order that nature should exist, a degree of permanence attached to them, such, that they become virtually unalterable elements, otherwise affinity could no longer act to produce the results we see.

Even if our elements, therefore, be compound, or otherwise transmutable, it is evident that we are not intended to have the power of decomposing or transmuting them. Such is the doctrine we have for many years taught in our lectures.

ALCALOIDS OR ORGANIC BASES.

These names are given to a class of nitrogenised organic compounds which, in their relations, are quite analogous to ammonia, or to oxide of ammonium. They are to be distinguished from such basic oxides as oxide of ethyle, oxide of methyle, &c., which contain no nitrogen, and, although they form neutral compounds with acids, yet exist in a peculiar state in these compounds, which cannot be

decomposed, like ordinary salts, by double decomposition. Thus, oxalate of oxide of ethyle does not precipitate with nitrate of lime, and chloride of ethyle does not decompose nitrate of silver. But the case is quite different with the alcaloids; for their salts undergo the same decomposition as those of ammonia.

Most of the alcaloids are found in vegetable juices, seeds, or roots; these are called vegetable alcalies, and they are generally the active principles of the plants, for the most part poisonous, in which they are found. But of late, organic bases quite analogous to those produced by nature, have been formed in a variety of processes; as, for example, the singular bases containing platinum; the bases containing arsenic, or arsenic and platinum; the bases of coal-tar, of which aniline, formed in several different processes, is one; the bases, chloraniline, &c., derived from aniline; the bases derived from oil of mustard; those derived from the decomposition of natural alcaloids, as *chinoline* and *colarnine*; those formed by the action of potash on melam, as melamine and ammeline; those produced by the action of ammonia on oil of bitter almonds and analogous bodies, such as amarine, lophine, picrine, and furfurine; those formed by the action of sulphide of ammonium on certain nitrogenised bodies, as aniline from nitrobenzole, naphthalidine from nitro-naphthalese, thialdine from aldehydammonia, &c.; those derived from creatine by the action of acids and bases, namely, creatinine and sarcosine; and such as are formed by the action of acids and bases on other animal compounds, of which glycocine is an example, being formed from gelatine by the action of potash, and from hippuric acid by the action of hydrochloric acid. The number of artificial bases has of late been very greatly augmented by the discoveries of Wurtz and of Hofmann, who have shown that an almost unlimited number of such bases, homologous with ammonia, may be obtained. Some of these have been already mentioned under the benzoic and ethylic series of compounds, and many more remain to be noticed. Most of these artificially formed bases are of very recent discovery, and it is evident that they must throw much light on the theory of the production of the natural alcaloids, and that the careful study of this part of the subject will, in all probability, eventually lead to the artificial formation of the natural organic bases.

The alcaloids possess, for the most part, very decided basic properties; when dissolved they act on vegetable colors like the inorganic alcalies; and they neutralise the strongest acids completely, generally forming crystallisable salts. Most of them, at the ordinary temperature, are expelled from their salts by ammonia, but many of them, at the heat of boiling water, expel ammonia from its salts, owing to the volatility of the latter alcali.

Their basic properties are not derived from the oxygen they contain, for no variation in the amount of that element affects their neutralising power. On the other hand, there is every reason to be-

lieve that their basic character depends on the nitrogen they contain; for they all, without exception, contain nitrogen, though several are devoid of oxygen. Moreover, most, if not all, of those which have been formed artificially, are prepared with the aid of ammonia, or some compound of ammonia, or amidogen. Before proceeding to describe them, we shall premise some general observations on the formation and constitution of artificial organic bases.

ON THE FORMATION AND CONSTITUTION OF ARTIFICIAL ORGANIC BASES.

Within the last few years, this is the department of organic chemistry which has made the greatest progress, and has yielded the most surprising results. Several theories had been started as to the constitution of the natural alcaloids, and Berzelius warmly advocated one of these, namely, that the alcaloids were coupled compounds, in which ammonia was coupled with other compounds. Taking aniline, $C_{11}H_7N$, as an example (for aniline, although an artificial base, is closely analogous to nicotine and conine, which are natural bases), Berzelius conceived aniline to be ammonia coupled with $C_{11}H_7$; thus $(C_{11}H_7) + NH_3 = C_{11}H_7N$. He supposed its neutralising power to depend on its ammonia; just as, in a coupled acid, the attached copula has no influence on the neutralising power. As all bases contained nitrogen and hydrogen, this view was possible, although none of them gave any signs of containing ammonia ready formed. On this and on other accounts, Liebig objected to this view, and proposed another, namely, that the organic bases were bodies in which amide, NH_2 , was combined with some compound, replacing the third equivalent of hydrogen in ammonia. To this he was led by considering ammonia as the hydride of amidogen or amide; as $NH_3 + H = AdH = NH_3$. Hence he viewed aniline as amide *plus* phenyle, $C_{11}H_7$. $NH_2 + C_{11}H_7 = AdPh = C_{11}H_7N$. And in a memoir published in 1839, he ventured to predict, that means would be found of substituting other compound radicals for the third atom of hydrogen in ammonia. Nay, he went so far as to say, that if ever the radicals, ethyle and methyle, should be thus substituted for hydrogen, the resulting compounds would be, without the least doubt, bodies perfectly analogous in properties to ammonia; that is, powerful volatile bases, but less volatile than ammonia. A more remarkable prediction was never ventured in chemistry, and it has been absolutely fulfilled; for, in 1849 Wurtz obtained the predicted compounds, methylamine, $C_2H_5N = AdMe$, and ethylamine, $C_4H_9N = AdAe$, and found them to be precisely what Liebig had anticipated ten years before; indeed, so like ammonia, that it is now certain that these bases had frequently occurred, and been taken for ammonia, from the resemblance of their smell to that of ammonia. This remarkable discovery of Wurtz has led to the further discovery, both by himself, by

Hofmann, and others, of a vast number of similar bases. Besides this, in the interval between the prediction and its fulfilment, many others had been discovered, chiefly by Hofmann, all of which tended to establish Liebig's views. Such were the substitution bases from aniline, the bases homologous with aniline, toluidine, cumidine, &c., and others, so that the theory of Liebig became at last firmly established. But the march of discovery did not stop here, for Hofmann soon ascertained that it applied only to one class, a very large class of artificial bases, and that bases could be formed, in which no amide was or could be present. In short, it appeared that not only the third eq. of hydrogen in ammonia, but with it one or both of the others, might be replaced by very many radicals, without destroying the basic character. Hofmann thus establishes the existence of three distinct series of bases, all derived from ammonia by substitution, and all analogous to it in properties, being volatile bases. If we make X, Y, and Z any three compound radicals, whether of the same or of different series, then we have

1. Amide bases.... $N H_3 + R$ (R being either hydrogen or a compound radical.)
 Ammonia $N H_3 + H$
 New bases..... $N H_3 + X$, or $N H_3 + Y$, or $N H_3 + Z$
2. Imide bases $N H + R_2$ ($N H =$ Imide)
 Ammonia $N H + H_2$
 New bases..... $N H + X Y$, or $N H + Y Z$, or $N H + X Z$
3. Nitryle bases ... $N + R_3$
 Ammonia $N + H_3$
 New bases..... $N + X Y Z$, or $N + X X Z$, or $N + Y Y Z$; or $N + X Z Z$,
 or $N + Y Z Z$; or $N + Y X X$; or $N + Y Y X$.

Here is at once a wide extension of the original view of Liebig as to the constitution of organic bases; and, whatever be their real constitution, bases are now known, belonging to each of the above series: that is, bases, the formula of which may be thus interpreted, and which are really obtained from compounds believed to contain the radicals supposed to be present in the bases.

Of the amide bases, many are known. The following are a few:

Ammonia	$N H_3 + H = H_3$	$N = Ad H$
Methylamine	$N H_3 + C_1 H_3 = C_1 H_3$	$N = Ad Me$
Ethylamine	$N H_3 + C_2 H_5 = C_2 H_5$	$N = Ad Ae$
Propylamine	$N H_3 + C_3 H_7 = C_3 H_7$	$N = Ad Pr$
Butylamine	$N H_3 + C_4 H_9 = C_4 H_9$	$N = Ad Bu$
Amylamine	$N H_3 + C_5 H_{11} = C_5 H_{11}$	$N = Ad Ayl$
Caprotylamine	$N H_3 + C_6 H_{13} = C_6 H_{13}$	$N = Ad Cp$
Phenylamine. Aniline.....	$N H_3 + C_6 H_5 = C_6 H_5$	$N = Ad Ph$
Tolylamine. Toluidine....	$N H_3 + C_7 H_7 = C_7 H_7$	$N = Ad To$
Xylamine, Xylidine.....	$N H_3 + C_8 H_9 = C_8 H_9$	$N = Ad X$
Cumidine	$N H_3 + C_9 H_{11} = C_9 H_{11}$	$N = Ad Cu$
Cymidine	$N H_3 + C_{10} H_{13} = C_{10} H_{13}$	$N = Ad Cym$

All these are known, and many more will soon be formed, especially in the ethyle series. Indeed, Fridau has obtained the compound, cetylamine, $C_{22} H_{45}$, $N = N H_3 + C_{21} H_{42} = Ad Ctl$, although it has no basic characters, or very feeble ones.

The following are the names of a few imide bases :

Ammonia	$N H + H_2$	$= H_2 N = Id, H_2$
Dimethylamine	$N H + 2 (C_2 H_5)$	$= C_4 H_7 N = Id, Me_2$
Diethylamine	$N H + 2 (C_4 H_9)$	$= C_8 H_{11} N = Id, Ae_2$
Diamylamine	$N H + 2 (C_{10} H_{21})$	$= C_{20} H_{33} N = Id, Ayl_2$
Diphenylamine	$N H + 2 (C_{12} H_5)$	$= C_{24} H_{11} N = Id, Ph_2$
Methylophenylamine	$N H + C_2 H_5 + C_{10} H_5$	$= C_{14} H_{15} N = Id, Me Ph$
Ethylophenylamine	$N H + C_4 H_9 + C_{10} H_5$	$= C_{18} H_{17} N = Id, Ae Ph$
Amylophenylamine	$N H + C_{10} H_{21} + C_{12} H_5$	$= C_{22} H_{21} N = Id, Ayl Ph$

All the above have been discovered and described by Hofmann. They are all volatile bases, analogous to ammonia.

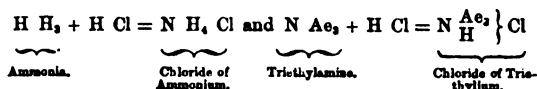
Of nitryle bases the following will serve as an example :

Ammonia	$N + H_2$	$= H_2 N = N, H_2$
Trimethylamine	$N + 3 (C_2 H_5)$	$= C_6 H_9 N = N, Me_3$
Triethylamine	$N + 3 (C_4 H_9)$	$= C_{12} H_{15} N = N, Ae_3$
Triamylamine	$N + 3 (C_{10} H_{21})$	$= C_{30} H_{33} N = N, Ayl_3$
Triphenylamine	$N + 3 (C_{12} H_5)$	$= C_{36} H_{15} N = N, Ph_3$
Amylo-diethylamine	$N + C_{10} H_{21} + 2 (C_4 H_9)$	$= C_{26} H_{23} N = N, Ae_2 Ayl$
Methylethylamine	$N + C_2 H_5 + C_4 H_9 + C_{10} H_{21}$	$= C_{16} H_{15} N = N, Me Ae Ayl$
Diethylophenylamine	$N + 2 (C_4 H_9) + C_{12} H_5$	$= C_{20} H_{15} N = N, Ae_2 Ph$
Methylethylophenylamine	$N + C_2 H_5 + C_4 H_9 + C_{12} H_5$	$= C_{18} H_{15} N = N, Me Ae Ph$
Diamylophenylamine	$N + 2 (C_{10} H_{21}) + C_{12} H_5$	$= C_{32} H_{17} N = N, Ayl_2 Ph$
Ethylamylophenylamine	$N + C_4 H_9 + C_{10} H_{21} + C_{12} H_5$	$= C_{26} H_{21} N = N, Ae Ayl Ph$

All of these, except triphenylamine, have been already obtained by Hofmann. It will be seen that the whole three series may be included under one head, namely, that of bases, corresponding to ammonia, in which one, two, or all three of the eqs. of hydrogen in ammonia have been replaced by one, two, or three different radicals; and that the amide, imide, and nitryle bases are the subdivisions of this group. Now there are two strong reasons for believing such to be the constitution of these bodies; 1st, that they are all analogous in properties to ammonia, and 2dly, that they are obtained by the action of ammonia on compounds of the radicals, methyle, ethyle, amyle, and phenyle; so that their formation and properties could be, and were predicted. It is obvious, therefore, that Liebig's views is only true of one of the subdivisions, the amide bases, and must be extended so as to include the two others.

But Hofmann has gone further still. He has discovered that, to the nitryle bases, such as triethylamine, $N + 3 (C_4 H_9) = C_{12} H_{15} N$, another equivalent of ethyle, &c., may be added, and a new series of bases obtained, corresponding not to ammonia, but to oxide of ammonium, $N H_4 O$, and resembling, in their properties, oxide of potassium or potash, much more than ammonia, as they are not volatile without decomposition. Oxide of ammonium is the same thing as ammonia *plus* water; and if, as is probable, oxide of ammonium does exist in the salts of ammonia, such as sulphate of ammonia, $N H_4 O, S O_3$, it is resolved into ammonia and water, as soon as separated. Such is also the case with the metals belonging to the three first series of ammonia bases (for being analogous to ammonia, they

form, with hydrogen, metals like ammonium). Thus, to take one example, triethylamine, with hydrochloric acid, forms chloride of triethylium, just like ammonia with the same acid.



And in sulphate of triethylamine, we have the oxide of the metal, as in sulphate of ammonia.



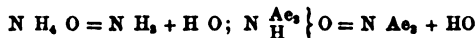
And this oxide, like that of ammonium, is resolved when separated into water and triethylamine.

But with the new or fourth series of bases it is different. The oxide of the metal is not resolved into other products, when separated from the acid, but can exist in a separate form. We have, first,

Ammonia.....	N H ₃	Triethylamine.....	N Ae ₃
Ammonium.....	N H ₄	Tetrethylum.....	N Ae ₄
Oxide of ditto.....	N H ₄ O	Oxide of ditto.....	N Ae ₄ O
Chloride of ditto.....	N H ₄ Cl	Chloride of ditto.....	N Ae ₄ Cl

While oxide of ammonium is instantly resolved into ammonia and water, oxide of tetrethylum is permanent, and much resembles potash.

Here, then, is a totally new series of bases representing, not ammonia, but oxide of ammonium, and therefore containing oxygen. If oxide of tetrethylum were as unstable as oxide of ammonium does ammonia and water; thus: $\text{N H}_4 \text{ O} = \text{N H}_3 + \text{H O}$. $\text{N Ae}_4 \text{ O} = \text{N Ae}_3 + \text{Ae O}$. Evidently, in the former case, the affinity of oxygen for hydrogen breaks up the oxide; but in the latter the affinity of oxygen for ethyle is not powerful enough to do so at the ordinary temperature. But where an atom of hydrogen is present in the same place as the fourth atom in ammonium, it is separated as water, as we have seen in triethylum, the oxide of which, like that of ammonium, cannot exist in the separate form. Thus,



These considerations explain how it happens that the oxides of the new organic metals, analogous to ammonium, are permanent. And it is worthy of notice, as a strong proof that these new compounds represent ammonium in which hydrogen has been entirely replaced by one, two, three, or even four different radicals, that it

has not been found possible to replace by these radicals more hydrogen than 4 equivalents, evidently the four of ammonium, N H_4 . Should any further replacement of hydrogen by ethyle, for example, occur, then either the group will be broken up, or the replacement will affect the radical itself; that is, if in tetrethylum we could replace an atom of hydrogen by ethyle, it would be an atom in one of the atoms of ethyle, which one might then become $\text{C}_4 \begin{Bmatrix} \text{H}_4 \\ \text{Ae.} \end{Bmatrix}$. But this is not very likely. The following table gives the hydrated oxides of the bases already discovered in the ammonium series :

Hydrated oxide of		
Ammonium	$\text{N H}_4 \text{ O, H O}$	$= \text{N H}_5 \cdot 2 \text{ H O}$
Tetramethylum	$\text{N Me}_4 \text{ O, H O}$	$= \text{C}_5 \text{ H}_{12} \text{ N, O, H O}$
Tetrethylum	$\text{N Ae}_4 \text{ O, H O}$	$= \text{C}_{16} \text{ H}_{20} \text{ N, O, H O}$
Methylotriethylum	$\text{N Me Ae}_3 \text{ O, H O}$	$= \text{C}_{14} \text{ H}_{18} \text{ N, O, H O}$
Amylotriethylum	$\text{N Ae}_3 \text{ Ayl O, H O}$	$= \text{C}_{22} \text{ H}_{26} \text{ N, O, H O}$
Tetramylum	$\text{N Ayl}_4 \text{ O, H O}$	$= \text{C}_{40} \text{ H}_{44} \text{ N, O, H O}$
Methylodiethylamylum	$\text{N Me Ae}_2 \text{ Ayl O, H O}$	$= \text{C}_{20} \text{ H}_{24} \text{ N, O, H O}$
Triethylphenylum	$\text{N Ae}_3 \text{ Ph O, H O}$	$= \text{C}_{24} \text{ H}_{20} \text{ N, O, H O}$
Methylethylamylophenylum ..	$\text{N Me Ae Ayl Ph O, H O}$	$= \text{C}_{28} \text{ H}_{34} \text{ N, O, H O}$

The general character of these bases is well marked. Like oxide of ammonium, and unlike the ammonia bases, they all have an even number of equivalents of hydrogen. The hydrates crystallise and are very soluble in water. They cannot be distilled without decomposition. Like potash, they attract carbonic acid from the air, have a caustic taste, and saponify oils. But they, and all their salts, are very bitter. Their iodides, chlorides, &c., contain the compound metals in union with iodine, &c., and resemble iodide of potassium. Thus hydriodic acid acts on the oxide of tetrethylum, yielding water and the iodide, just as it acts on oxide of potassium.



Here, then, it will be seen, we have four large series of bases, evidently representing, three of them ammonia, the fourth, oxide of ammonium; and it is highly probable that many of the natural bases belong to these four series. As, however, the ammonia bases of all three series are volatile, so we can only at present refer to that class the volatile natural bases, such as coniine and nicotine. But the ammonium bases agree with the non-volatile natural bases in four points: first, in being fixed; second, in containing oxygen; third, in having a bitter taste; and fourth, in yielding volatile bases when decomposed by heat. Some of the formulæ in the last column of the last table approach very nearly to those of natural fixed organic bases. In fact, an attempt was made by Hofmann to form artificially a natural base, quinine. The formula of quinine, according to the best analyses, is $\text{C}_{20} \text{ H}_{18} \text{ N O}_7 = \text{C}_{20} \text{ H}_{11} \text{ N O, H O}$. When heated, it yields a volatile base, quinoline. Now this was supposed

to be $C_{12}H_8N_2$, and quinine to differ from it by $C_2H_4O_2$. And the hydrated oxide of tetramethylum, a bitter fixed base, $C_4H_{12}NO_2 = C_2H_4N_2O, H_2O$, yields, when heated, a volatile base, trimethylamine, C_3H_9N ; the difference being, as before, $C_2H_4O_2$. Now as trimethylamine may be reconverted into the hydrated oxide of tetramethylum by the action of iodide of methyle on it, and of oxide of silver on the iodide thus produced, the question was asked, May not quinoline, which is found in coal-tar, yield quinine in the same way? In point of fact, the action of iodide of methyle on quinoline does yield a crystallised iodide, apparently similar to the hydriodate of quinine, but as recent researches show, not even isomeric with it; the true formula of quinoline being $C_{10}H_7N$. Still we may hope to succeed in process of time in forming artificially the natural bases.

But we must not suppose that Liebig's theory, even as extended by Hofmann, so as to include, besides amide bases, imide, nitrile and ammonium bases, includes all the possible modes of formation of organic bases. Some may be, as Berzelius imagined, coupled ammonias, some coupled amide, imide, nitrile, or ammonium bases, or substitution products derived from these. And it must be borne in mind, that even of these four series of bases we have only learned to know those containing the four radicals, methyle, ethyle, amyle, and phenyle, while there may be hundreds of similar radicals. The field has been opened; it remains for us to cultivate it. Of the bases mentioned above, many have been already described under the ethylic series of radicals, and the remainder will be noticed under aniline or phenylamine, further on.

Besides the methods employed for the production of the bases of the four classes above mentioned, chiefly the action of the bromides or iodides of methyle, ethyle, &c., on ammonia, there are various other processes which yield artificial organic bases, which must here be briefly noticed. Bases, then, are formed:

1. By the action of ammonia on organic products, aided by other processes. Thus ammonia forms bases, as we have seen, with oil of bitter almonds and furfurole, when aided by the subsequent action of potash; with oil of mustard; and probably in other instances.

2. In the destructive distillation of nitrogenised animal and vegetable matters, such as albuminous compounds, natural bases, indigo, and coal. In Dippel's animal oil are found bases of three, if not four, distinct series; those of methylamine, &c., of aniline, of picoline, isomeric with that of aniline, and the series of pyrrole bases. (Anderson.) Indigo yields aniline; morphine, narcotine, codeine, quinine, cinchonine, strychnine, and pelosine, yield volatile bases when heated; and the oil of coal-tar contains various bases of the methylamine series, of that of aniline, and perhaps of others.

3. By the action of sulphuretted hydrogen on compounds of am-

monia. Thialdine, a very remarkable base, is formed by the action of sulphuretted hydrogen on aldehydammonia.

4. By the action of sulphuretted hydrogen, or of sulphide of ammonium on substitution compounds containing N O_4 ; as when aniline is formed in this way from nitrobenzole, nitraniline from dinitrobenzole, or toluidine from nitrotoluole.

5. By heating nitrogenised compounds with potash or baryta; as when aniline is formed by heating isatine with potash, chloraniline by heating chlorisatine with potash, melamine and ammeline by heating melam with potash, and sarcosine by heating creatine with baryta.

6. By heating organic compounds with acids; as when glycocine is formed by boiling hippuric acid with hydrochloric acid; creatinine from creatine; and alanine from a mixture of aldehydammonia, hydrocyanic acid, and hydrochloric acid.

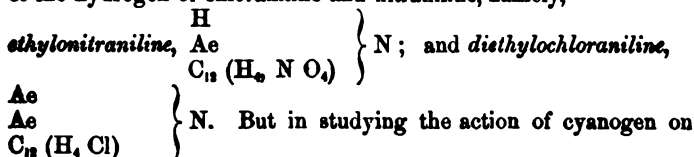
7. Lastly, by spontaneous metamorphosis, as when hydrated cyanate of ammonia passes into urea, or cyanate of methylamine into methylo-urea, when their solutions are evaporated.

Of all of these methods, examples will be given under the individual bases. Of the production of the four classes of bases, amide, imide, nitrile, and ammonium bases, with the radicals of the ethyle series, numerous examples have already been given.

It is to be observed, that we have already succeeded in forming artificially three natural bases, all of animal origin, namely, urea, glycocine, and creatinine. In other cases, as Hofmann's new base, methylo-quinoline, turns out not to be quinine, we have only, as yet, produced bases closely analogous to natural bases. Thus furfurine, an artificial base, is used, like quinine, as an anti-periodic; and the bitter ammonium bases of Hofmann will most probably be found powerful remedies, possibly of that class.

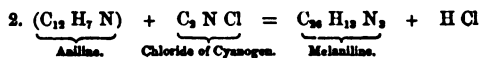
Lastly, in the formation of artificial bases, we have succeeded in several, indeed in many cases, in imitating the natural process of building up complex atoms or molecules from such as are less complex. This is seen in the long list of Hofmann's bases; and also in furfurine, produced by the coalescence of 2 eqs. of furfuramide; and amarine, formed by the coalescence of 3 eqs. of oil of bitter almonds along with ammonia. It has hitherto been found comparatively easy to break up or resolve into simpler forms the complex natural organic compounds; but now we begin, like nature, to construct the complex from the more simple: perhaps, in its ultimate results, the most important step yet made in advance in organic chemistry. Our methods are still coarse and violent compared with those of nature, which are gentle but irresistible, and infinitely varied in their results; but yet we are able to imitate nature, and to replace one group by another, and thus to form a series of artificial products, running parallel, in many instances, with the natural ones, and exhibiting precisely similar properties.

The labors of Hofmann have resulted in the production of several substitution compounds from aniline. These are principally basic, and are termed, chloraniline, dichloraniline, trichloraniline, bromaniline, dibromaniline, tribromaniline, and nitraniline. Hofmann has also obtained bases, in which ethyle is substituted for part of the hydrogen of chloraniline and nitraniline, namely,

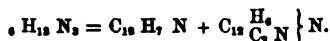


Cyaniline. When cyanogen gas is made to act on an alcoholic solution of aniline, crystals are formed, which contain several bodies. One of these is a base, *cyaniline*, which is $\text{C}_{14} \text{H}_7 \text{N}_3 = \text{C}_{12} \text{H}_7 \text{N} + \text{C}_2 \text{N}$. Here the cyanogen has combined with aniline to form the new base. It forms brilliant silvery scales, very sparingly soluble in any liquid. It forms salts with acids, which are permanent in the dry state, but easily decomposed in solution.

Melaniline. When gaseous chloride of cyanogen acts on aniline, there is formed the hydrochlorate of this base. The base itself is crystalline, and has the formula $\text{C}_{26} \text{H}_{13} \text{N}_3$. It is thus formed—



It may be regarded as aniline, coupled with a compound, which is aniline, in which 1 eq. of hydrogen has been replaced by cyanogen. Thus,



Melaniline is very sparingly soluble in water, but soluble in alcohol and ether. It forms crystallisable salts with acids. With chlorine it yields the hydrochlorate of a new base, *dichloromelaniline*, $\text{C}_{26} \frac{\text{H}_{11}}{\text{Cl}_2} \left\} \text{N}_3$; with bromine, *dibromomelaniline*, $\text{C}_{26} \frac{\text{H}_{11}}{\text{Br}_2} \left\} \text{N}_3$; and with iodine, *diiodomelaniline*, $\text{C}_{26} \frac{\text{H}_{11}}{\text{I}_2} \left\} \text{N}_3$. With nitric acid it yields the base *dinitromelaniline*, $\text{C}_{26} \frac{\text{H}_{11}}{2 \text{N O}_4} \left\} \text{N}_3$; and with cyanogen, it forms a compound in which 1 eq. of melaniline is united with 2 of cyanogen, analogous to cyaniline, and called *dicyanomelaniline*; but this is not, like the other four, a substitution product. It may be viewed as composed of 1 eq. cyaniline, 1 eq. of the compound $\text{C}_{12} \frac{\text{H}_6}{\text{Cy}} \left\}$, supposed to exist in melaniline, and 2 eqs. of cyan-

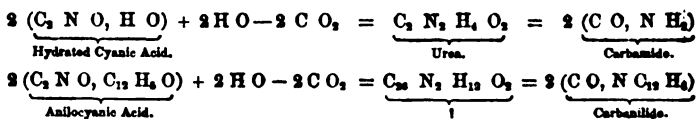
ogen, as if each of the groups in melaniline took up, like aniline itself, 1 eq. of cyanogen. Its formula is $C_{20} H_{12} N_8 = C_{20} H_{12} N_8 + 2 C_2 N = (C_{14} H_8 N_4 + C_2 N) + (C_{12} H_4 N_4 \left. \begin{smallmatrix} H_2 \\ C_2 N \end{smallmatrix} \right\} N + C_2 N)$. It is a feeble base.

With diluted acids, cyaniline yields various products, among which are *oxamide*, *oxanilide*, analogous to oxamide, and a compound of both, *oxanilamide*. Oxanilide is $C_{12} H_8 N_4 C_2 O_2$, and oxanilamide is $C_{12} H_8 N_4 C_2 O_2 + H_2 N_2 C_2 O_2 = C_{16} N_6 H_8 O_4$.

When dicyanomelaniline, $C_{20} H_{12} N_8$, is boiled with acids, it undergoes a remarkable change, and yields a yellow product, $C_{20} H_{12} N_8 O_4$. Thus, $C_{20} H_{12} N_8 + 4 H O + 2 H Cl = 2 (N H_4 Cl) + C_{20} H_{12} N_8 O_4$. It may be regarded as binoxalate of melaniline, *minus* 4 eqs. of water. This is the composition of an imide, and the compound has been named Melanoximide. When heated, the body yields, among other products, a volatile liquid, boiling at 35.3° , of a very pungent odor, $C_{14} N H_4 O_2$, which bears to hydrated cyanic acid the same relation as aniline does to ammonia. $C_{12} H_7 N = N H_2 + C_{12} H_4$. $C_{14} N H_4 O_2 = C_2 N O, H O + C_{12} H_4$. Hence it is named *Anilocyanic Acid*. With acids and bases it is resolved into aniline and carbonic acid, just as cyanic acid into ammonia and carbonic acid, $C_{14} N H_4 O_2 + 2 H O = C_{12} H_7 N + 2 C O_2$. In short, it is hydrated cyanic acid, in which the hydrogen of its basic water is replaced by phenyle, $C_{12} H_4$, or it is the cyanate of oxide of phenyle.



As cyanic acid with water yields, first ammonia and carbonic acid, and then, by the action of this on another portion of the acid, cyanate of ammonia or urea, so anilocyanic acid, with water, yields first aniline and carbonic acid, and secondly cyanate of aniline, or 2 atoms of *carbanilide*, analogous to urea, which is 2 atoms of carbamide.



Carbanilide is therefore urea, in which 2 eqs. of hydrogen are replaced by phenyle, $C_{12} H_4$, diphenyl-urea; but it is uncertain whether it may not be only polymeric with the true diphenyl-urea; that is, whether 1 eq. of the latter may not resolve itself into 2 eqs. of carbanilide. There is another compound, carbamide-carbanilide, in which 1 eq. of hydrogen in urea is replaced by 1 of phenyle. This is phenyle-urea, and is formed when anilocyanic acid acts on ammonia. $C_2 N O, H O + N H_3 = C_2 H_4 N_2 O_2$, and $C_2 N O, C_{12} H_4 O + N H_3 = C_{14} N_2 H_6 O_2$.

When cyanic acid acts on alcohol it yields two compounds, urethane or carbamate of oxide of ethyle, and allophanate of oxide of ethyle, according as 1 or 2 eqs. of the acid act on 1 of alcohol. Hofmann finds that anilocyanic acid produces with the known alcohols compounds analogous to urethane, and probably also compounds analogous to allophanic ether. As urethane contains carbamic acid, so the phenyl-urethane must contain an acid in which 1 eq. of hydrogen in carbamic acid is replaced by phenyle. Now, carbamic acid is $C_2 N H_3 O_2, H O$, and the new acid must be $C_2 N \begin{matrix} H \\ C_6 H_5 \end{matrix} \left. \begin{matrix} \\ \\ \end{matrix} \right\} O_2, H O = C_{14} N H_5 O_2, H O = C_{14} N H_5 O_4$. This is the formula of anthranilic or carbanilic acid; but whether the acid in phenyl-urethane or carbanilate of oxide of ethyle be identical or only isomeric with anthranilic acid from indigo, is not yet known.

The reader will not fail to observe that, as the cyanates of oxides of ethyle, methyle, &c., when heated with potash, yield ethylamine, methylamine, &c., so we may expect the anilocyanates or phenylcyanates of the oxides of ethyle, &c., to yield with potash a new series of bases, in which 1 eq. of the hydrogen of aniline is replaced by ethyle, methyle, &c. Here also aniline will probably retain its analogy to ammonia; but the investigation is very difficult, from the long, tedious, and expensive processes necessary to obtain first aniline, then melaniline, dicyano-melaniline, and anilocyanic acid, with which last it must be commenced.

The reader is referred to Dr. Hofmann's papers for many interesting details and ingenious speculations, which we are compelled here to omit.

When melaniline is heated it yields, among other products, a body called aniline-mellone, which, however, combines with aniline to yield the compound $C_{14} H_{11} N_7 = 3 (C_6 H_5 N) + C_{18} H_4 N_4$. The latter group is anilomellone. Laurent has obtained a compound $C_{30} H_{11} N_6$, which is $= C_{18} H_4 N_4 + C_{12} H_3 N_2$. Anilomellone, or phenylomellone, $C_{18} H_4 N_4$ is mellone, $C_6 N_4$, coupled with $C_{12} H_4$, or phenyle, minus H.

Besides the above derivatives from aniline, there are many in which phenyle is substituted for hydrogen; as, for example, volatile bases, like those of the series of ethylamine, aniline itself being the first of them; in the others we have the hydrogen of ammonia replaced to the extent of two, three, or four eqs., either by phenyle, or by phenyle in part, and in part by one or more of the ethylic radicals. Of these, the following are known:

Ethylophenylamine or *Ethylaniline*, $C_{18} H_{11} N = N, H Ae Ph$. This base is obtained by the action of bromide of ethyle on aniline. $N H_2 Ph + Ae Br = H Br + N H Ae Ph$. Its empirical formula is $C_{14} H_{11} N$. It much resembles aniline.

Diethylophenylamine, $C_{20} H_{13} N = N, Ae_2 Ph$, is formed when the

preceding base is acted on by bromide of ethyle. It resembles the foregoing.

Triethylophenylium. The iodide of this compound is formed when iodide of ethyle acts on the preceding base, $N\text{ Ae, Ph} + \text{Ae I} = N\text{ Ae, Ph, I}$. It forms, like the other ammonium bases, a hydrated oxide, which is a powerful base.

Methylethylamylophenylium. This sesquipedalian word denotes an ammonium compound, the iodide of which is formed when iodide of methyle acts on ethylamylophenylamine, $\text{Me I} + N\text{ Ae Ayl Ph} = N, \text{Me Ae Ayl Ph} + \text{I}$. Its hydrated oxide is, like the preceding one, a powerful base.

Ethylamylophenylamine, $N, \text{Ae Ayl Ph}$, is obtained by the action of bromide of amyle on ethylophenylamine, or of the bromide of ethyle on amylophenylamine. $N, \text{H Ae Ph} + \text{Ayl Br} = N, \text{Ae Ayl Ph} + \text{H Br}$, or $N, \text{H Ayl Ph} + \text{Ae Br} = N, \text{Ae Ayl Ph} + \text{H Br}$.

Methylophenylamine, $N, \text{H Me Ph}$; *Methylethylophenylamine*, $N, \text{Me Ae Ph}$; *Amylophenylamine*, $N, \text{H Ayl Ph}$; *Diamylophenylamine*, $N, \text{Ayl, Ph}$ —are all formed by means of analogous processes, and are all volatile bases. It is singular that the two last-named have a strong and fragrant smell of roses.

METHYLE AND ETHYLE.

Since the last edition of this work went to press, the above two radicals have been isolated and studied.

Methyle was first obtained by Frankland and Kolbe, as a product of the action of potassium on cyanide of ethyle. It was soon after observed by Kolbe among the products of the electrolytic decomposition of acetic acid; and by Frankland, among the products of the action of zinc, aided by heat and under pressure, on iodide of ethyle, and by the action of water on the new radical zincethyle. In all these cases it is accompanied by other products, all of which are not exactly known; but in the third of them it seems to be formed in the following manner: iodide of ethyle, $\text{C}_2\text{H}_5\text{I}$, acted on by zinc, yields iodide of zinc, Zn I_2 , and ethyle, C_2H_5 ; and a part of the ethyle is resolved into methyle and elayle, thus: $\text{C}_2\text{H}_5 = \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2$.

Methyle is a gas, of Sp. G. 1.0365, which, at 0°F ., is not liquid, and which has resisted a pressure of 20 or 30 atmospheres. It is combustible, burning with a bluish flame and little light. It has an ethereal smell, and is not absorbed by water, but alcohol absorbs it. It has certainly the composition C_2H_3 , but we cannot be certain that it is the radical methyle, or that it may not be only isomeric with that body. Since, however, its production by the electrolysis of acetic acid is attended by that of oxide of methyle, we may conclude, for the present, that it is the true radical.

Methyle exists in nature, but not uncombined, so far as we yet know. Its oxide is found in the oil of *Gaultheria procumbens*, combined with salicylic acid. But oxide of methyle is more abundant and better known as one of the chief ingredients, in the form of hydrate, of the more volatile product of the distillation of wood.

Methyle is chiefly interesting as the lowest or first member of a very remarkable group of homologous radicals, the formulæ of a number of which are given in Column 1 of the table of homologous compounds. Immediately above it in the series (below it in the column) stands ethyle, C_2H_5 , which differs from it by C_2H_5 , and the same increase, of C_2H_5 , is made at each step. Now, if we subtract C_2H_5 from methyle, instead of adding them to it, we obtain H , or hydrogen, which is therefore the inorganic starting-point of this organic series. And we shall find that methyle and its homologues agree in many points with hydrogen. Thus they all combine, although not directly, with oxygen, chlorine, bromine, iodine, sulphur, cyanogen, &c., in the same proportions by volume as hydrogen does; they may be substituted for hydrogen in ammonia without changing the type of that base; and as hydrogen forms compounds with certain metals, tellurium, arsenic, and antimony, so also do methyle and ethyle. In one point of view, therefore, we may regard all the radicals of the methyle series as homologues of hydrogen. But we must remember that in another they differ; for while the oxide of hydrogen is neutral, that of methyle is basic: the chlorides, &c., of hydrogen are strong acids, while the chlorides, &c., of methyle are neutral ethers.

Another circumstance must be mentioned here. Most of the known compounds of carbon and hydrogen which are volatile have such a density in the form of gas, that their formula represents 4 vols.; that is, the densities of their elements, added together in the proportions indicated by the formula, represent the weight of 4 vols. of the compound, and this sum must be divided by 4 to give the density of the compound, which is the weight of 1 vol. But methyle and its homologues, if examined in reference to their density, are found to represent only 2 vols., a somewhat unusual occurrence. Thus methyle, C_2H_5 , represents not 4, but 2 volumes of the gas, which is therefore twice as heavy as it should be, if it followed the law of 4 volumes. For this reason, Hofmann and others are disposed to think that the formula of methyle should be doubled, which would give C_4H_{10} , and this, calculated for 4 volumes, would agree with the actual density of the gas. But it is certain that many things in the history of methyle agree better with the formula C_2H_5 , than with C_4H_{10} , for the latter would make the oxide $C_4H_6O_2$, the chloride $C_4H_8Cl_2$, &c., and would make it necessary to double the quantities of all those substances which act on it, thus yielding very improbable formulæ. The two opinions may be reconciled by supposing that, as Frankland has recently shown, the methyle produced

in the processes above mentioned is not identical in all of them. The methyle obtained from cyanide of ethyle by potassium, and that formed by the action of water on zincethyle, C_4H_6Zn , is not true methyle, but a polymeric compound, C_4H_6 , homologous with marsh-gas (methylole or formène, C_2H_2 , or rather C_2H_4): while the gas produced in the electrolysis of acetic acid is the true methyle, C_2H_2 . The former may be supposed to be produced by the coalescence of 2 atoms of the latter into one double molecule. The same remarks apply to ethyle, and the other radicals homologous with methyle, and will not, therefore, need to be repeated when treating of these.

When zincethyle, C_4H_6Zn , a body to be described hereafter, is acted on by water, there is formed oxide of zinc, and a gas is given off, which, as already mentioned, is either methyle, C_2H_2 , or the polymeric body, C_4H_6 , most probably the latter. Its formation is very simple, $C_4H_6Zn + H_2O = ZnO + 2(C_2H_2)$; or $C_4H_6Zn + H_2O = ZnO + C_4H_6$. If we adopt the latter formula, we may regard it as hyduret of ethyle, C_4H_6, H ; and the corresponding compound of methyle, which is formed when zincmethyle is acted on by water, will be C_2H_4 . Its formation will be as follows: $C_2H_4Zn + H_2O = ZnO + 2(C_2H_2)$; or $C_2H_4Zn + H_2O = C_2H_4$. The latter formula will become C_2H_6, H , or hyduret of methyle. Adopting this view, we have the two parallel and polymeric series, in each of which the members are homologous:

C_2H_2 , Methyle	$C_2H_4 = C_2H_6, H$, Hyduret of Methyle,
C_4H_6 , Ethyle	$C_4H_8 = C_4H_{10}, H$, Hyduret of Ethyle,
C_6H_8 , Propyle	$C_6H_{10} = C_6H_{12}, H$, Hyduret of Butyle,
	$C_{10}H_{14} = C_{10}H_{16}, H$, Hyduret of Caproyle,

and so on. It is highly probable that in each case both compounds exist, except in the first hyduret, that of methyle, which has no corresponding polymeric body in the first column, since such a compound would be C_2H_{10} , an impossible formula.

Ethyle. $C_4H_6 = Ae.$

This, the second radical of the methylic series (see table of homologous compounds) is obtained when iodide of ethyle is acted on by zinc, in closed tubes, at a high temperature, $C_4H_6I + Zn = ZnI + C_4H_6$. Part of the ethyle combines with another portion of zinc, to form zincethyle; part of it is resolved into methyle and elayle, thus $C_4H_6 = C_2H_2 + C_2H_4$; and part of it escapes unchanged. It is a colorless gas of a faint ethereal smell, burning with a bright white flame; its Sp. G. is 2.00394. At 32° , and under the ordinary pressure, it is not condensed; but under a pressure of $2\frac{1}{2}$ atmospheres it forms a mobile liquid. Alcohol absorbs it.

Ethyle is, in all respects, analogous to methyle, but, according to the law which regulates homologous series, its density is higher, while its volatility is less. Methyle is gaseous under a pressure of

20 atmospheres and upwards, but ethyle is easily condensed, and under the ordinary pressure, boils at 23° F. At the same time we must not forget that this compound, although it has the formula of the radical ethyle, may, like methyle, be possibly only an isomeric modification of the true radical. It does not exhibit strong affinities, and cannot be made directly to combine with oxygen, chlorine, &c.

Several new salts of the oxide of methyle have lately been discovered. The *carbonate of oxide of methyle* is formed when chloro-carbonic acid acts on pyroxilic, and the product $C_4 H_2 Cl O_4$ is mixed with ammonia. The oily product first produced, $C_4 H_2 Cl O_4$, is a compound of oxide of methyle with an acid, $C_2 O_2 \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\}$, and

may be represented thus, $C_2 H_2 O, C \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\}$. When it acts on ammonia, the latter is decomposed, 1 eq. of its hydrogen taking the chlorine of the oil, while the chlorine is replaced by oxide, and the resulting beautifully crystalline compound is the carbonate of oxide of methyle, $C_2 H_2 O, C \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\} + N H_3 = H Cl + C_2 H_2 O, C_2$

$O_2 \left\{ \begin{smallmatrix} O_2 \\ NH_2 \end{smallmatrix} \right\}$. This last group is carbonide, or carbonic acid, an acid amidide. The carbonide is isomeric with glycocine.

Phenomethole. SYN. Anisole: Carbolate of Oxide of Methyle. $C_{14} H_8 O_2 = C_2 H_2 O, C_{12} H_6 O$. This compound, apparently homologous with hydrated carboic acid, $C_{12} H_6 O_2$, is obtained by heating with baryta the preceding compound, or anisic acid, $C_{16} H_8 O_2, H O$, which is isomeric with it. $C_{16} H_8 O_2 + 2 Ba O = 2 (Ba O, C O_2) + C_{14} H_8 O_2$. Cahours has shown that this compound, which bears to anisic acid the same relation as phenole or carboic acid does to salicylic acid, is really the carbolate of oxide of methyle, or hydrated carboic acid, in which 1 eq. of water is replaced by 1 eq. of oxide of methyle. It is, therefore, not truly homologous with carboic acid, but is a compound of that acid with oxide of methyle, and is consequently the first member of a series of homologous compounds; thus,

1. Phenomethole..... $C_{14} H_8 O_2 = C_2 H_2 O, C_{12} H_6 O$.
2. Phenethole..... $C_{16} H_{10} O_2 = C_4 H_4 O, C_{12} H_6 O$.
3. Phenopropyle..... $C_{18} H_{12} O_2 = C_6 H_6 O, C_{12} H_6 O$.
4. Phenobutyle..... $C_{20} H_{14} O_2 = C_8 H_8 O, C_{12} H_6 O$.
5. Phenamyle..... $C_{22} H_{16} O_2 = C_{10} H_{10} O, C_{12} H_6 O$.

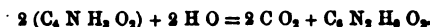
The compounds Nos. 3 and 4 have perhaps not yet been formed, but as propylic and butylic alcohols and ethers are now known, their formation may be with certainty predicted. The names given in the table are analogous to that of phenole (carboic acid) with which these compounds are apparently or empirically homologous, as carboic acid differs from No. 1 by $C_2 H_2$. These compounds, however,

cannot be truly homologous with carbolic acid, because they are not acids but neutral ethers, and their true names are, in full, carbolate of oxide of methyle, or of ethyle, propyle, butyle, amyle, and so on.

When salicylate of oxide of methyle is acted on by nitric acid, it yields nitrosalicylate of oxide of methyle, $C_7 H_5 O_2 C_{14} \left\{ \begin{smallmatrix} H_4 \\ NO_2 \end{smallmatrix} \right\} O_2$, in yellow silky prisms. With ammonia, this compound forms, like the corresponding ethyle compound (which see), nitrosalicylamide.

The mucate of oxide of methyle is a crystalline solid, analogous in its preparation and properties to the corresponding salt of ethyle.

Cyanate of Oxide of Methyle, $C_4 N H_5 O_2 = C_4 H_5 O, C_2 N, O$. This compound was obtained by Wurtz, by distilling cyanate of potash with sulphomethylate of potash (double sulphate of methyle and potash). It is a volatile liquid, of a very penetrating smell. With ammonia it yields a crystalline product, $C_4 N_2 H_5 O_2$, homologous with urea, and which may be called methylo-urea, since it is urea, in which 1 eq. of hydrogen is replaced by 1 eq. of methyle. Cyanate of oxide of methyle, in contact with water, is resolved into carbonic acid and a new compound, dimethylo-urea, isomeric with ethylo-urea.



Here we have another series of homologous compounds, not included in the table; but, indeed, every compound of methyle, and every derivative from it yet known, is, in like manner, the starting-point of an homologous series, and it will be seen that the table, large though it is, admits of enormous extension horizontally.

Allophanate of Oxide of Methyle, $C_4 N_2 H_5 O_2$. When the vapors of cyanic acid are brought in contact with pyroxilic spirit, this compound is formed. It is $C_4 H_5 O + C_2 N_2 H_5 O_2$. The latter group is allophanic acid, the production of which will be explained further on, under ethyle.

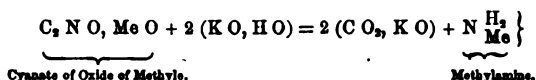
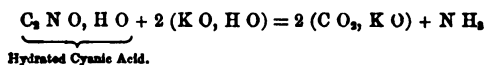
Cyanurate of Oxide of Methyle, $C_{12} N_3 H_5 O_6 = 3 C_2 H_5 O, C_2 N_2 O_2$. This compound, according to Wurtz, is formed when sulphomethylate of potash is heated with cyanurate of potash. It is a crystalline solid, fusible at 284° , and volatile at 563° . It is insoluble in water, soluble in alcohol and ether.

Many other salts of oxide of methyle might be enumerated, did space permit; but those already given suffice to show that oxide of methyle replaces the water of hydrated acids, just as oxide of potassium does; or rather, that methyle replaces the hydrogen of hydrated or of hydrogen acids, as metals do, yielding neutral compounds.

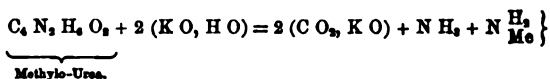
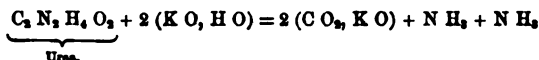
Before proceeding to the products derived by oxidation or other modes of decomposition from oxide of methyle or pyroxilic spirit, it may be as well here to point out the existence of compounds, in which methyle replaces the hydrogen of ammonia, without destroy-

ing its basic characters, compounds which are among the most remarkable which have been of late years discovered, and the discovery of which has very greatly added to our knowledge of the organic bases. They are here introduced, because the first of them was obtained from some of the salts described in the immediately preceding paragraphs, namely, from the cyanate of oxide of methyle, from the methylo-urea, and from the cyanurate, polymeric with the cyanate.

Methylamine. $C_2 H_5 N = N \begin{smallmatrix} H_2 \\ Me \end{smallmatrix} \}$. According to Wurtz, this compound is obtained by heating cyanate of oxide of methyle with potash. Bearing in mind that hydrated cyanic acid (from which this cyanate only differs in containing 1 eq. methyle, $C_2 H_5$ in place of 1 eq. hydrogen) is decomposed by potash, yielding carbonate of potash and ammonia, this change is readily explained by the following equations:



Since the cyanurate of oxide of methyle, which, as we have seen, is tribasic, is polymeric with the cyanate, its equivalent being exactly 3 times greater, we have only to multiply the last equation by 3 to explain the production of methylamine from the cyanurate. From methylo-urea it is obtained as follows, comparing the action with that of urea:



These equations show, that, as in the compounds employed, hydrogen has been replaced by methyle, $C_2 H_5$, so in the products the same substitution continues. And if we regard ammonia as the hyduret of amide, $N H_3, H$, then methylamine is methylamide, $N H_3, Me = N H_3, C_2 H_5 = C_2 H_5, N$.

Methylamine has also been observed among the products of decomposition of several organic compounds, such as morphine, codeine, caffeine, &c., and is probably a constituent of many natural products. It is found also in the oil obtained by distillation from animal matter.

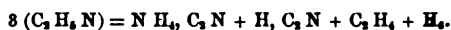
Methylamine is a condensable gas, of Sp. G. 1.075. At or a little below 32° , it forms a mobile liquid. It has a very pungent smell,

so like that of ammonia, that it has certainly been frequently taken for ammonia, when accidentally formed, and thus overlooked. It is, of all known gases, the most soluble in water. At 50° water takes up about 1150 times its volume of the gas. The smell of the gas and of its solution, although closely resembling that of ammonia, has yet something empyreumatic and peculiar. Methylamine is distinguished from ammonia by the property of kindling at a candle, and burning with a yellowish flame. Ammonia can only be kindled in oxygen gas.

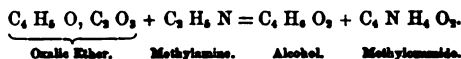
Methylamine is a very powerful base. It neutralises the strongest acids, and forms thick white vapors with the volatile acids, like ammonia. It acts on metallic solutions, as, for example, those of silver and copper, exactly like ammonia. The salts of methylamine are closely analogous to those of ammonia, and the bichlorides of platinum and mercury, and the terchloride of gold, form double salts, resembling the corresponding compounds of ammonia. Nay, when methylamine acts on protochloride of platinum, it gives rise to a series of bases perfectly homologous with those described under ammonia, but which our limited space forbids us to describe in detail.

When sulphate of methylamine is evaporated along with cyanate of potash, methylo-urea is obtained. It would appear that the body thus obtained has all the properties of a urea, and that the compound already described under that name is perhaps only an isomeric modification of it.

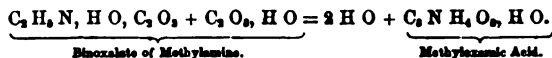
When heated strongly, methylamine is decomposed, yielding cyanide of ammonium, hydrocyanic acid, marsh-gas, and hydrogen. Thus :



Methyloxamide, $C_4 N H_4 O_3$. When the oxalate of methylamine, $C_4 H_8 N, H O, C_2 O_3$, is heated, it yields *methyloxamide*, homologous with oxamide. But this compound, like oxamide, is better obtained by the action of the base itself on oxalic ether.



Methyloxamic acid, $C_4 N H_4 O_3, H O$, is obtained, like oxamic acid, by heating the binoxalate of the base.



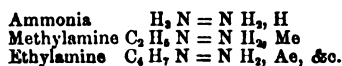
These two products are homologous with, and perfectly analogous to, oxamide and oxamic acid. Methyloxamide, however, is soluble in water.

It is hardly necessary to add, that for every neutral amide, such

as oxamide, benzamide, &c., as well as for every acid amide, such as oxamic acid, carbamic acid, &c., we may expect to have a corresponding compound, in which 1 eq. of hydrogen is replaced by methyle, or, what is the same thing, amidogen, N, H, H , is replaced by methylamidogen, N, H, Me .

Methylamine, when acted on by chlorine, bromine, and iodine, yields substitution products, which as yet have been little studied. Those of the corresponding base, ethylamine, appear to have lost the basic character, as will be explained further on. Here it is only necessary to state that methylamine does yield similar products.

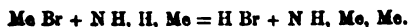
We have seen that methylamine is the first member of a series of bases, homologous with ammonia; and we may even regard ammonia itself as an organic base, and the true starting-point of the series, as hydrogen is of the series of radicals to which methyle belongs. The series will be seen in the last column of the table of homologous compounds, and it will be observed that, viewed as the starting-point of that series, ammonia is to be represented as hydramide, NH_2, H ; and that it is this last atom of hydrogen which is replaced by methyle and its congeners, so that we have



At each step $C_2 H_5$ is added—or, what is the same thing, in each base, amide, $N H_2$, is combined with methyle, $C_2 H_5$, ethyle, $C_4 H_7$, &c., &c., these radicals differing by $C_2 H_5$. This may be called the first series of bases, homologous with ammonia, or *amide bases*, since in them we have amide, $N H_2$, *plus* the radicals. The general formula of this series is either, Ad (amide) + $C_n H_{2n+1}$; or $C_n H_{2n+1}, N$. We shall see that a considerable number are known of this first or methylic series of amide bases, as well as several of a second or phenylic series also of amide bases, of which aniline (phenylamine) is the type. And doubtless other series will be discovered, still of *amide bases*.

But there are already known some series of bases homologous with ammonia, yet not *amide bases*, for our knowledge of which we are indebted to Hofmann. The first of these is that of the *imide bases* of the methylic radicals. The name *imide* is given to the compound $N H$, or amide *minus* hydrogen, which exists, combined, in certain derivatives of ammonia.

Now, to understand the formation of imide bases, ammonia must be viewed as $N H, H, H$; the group $N H$ being imide; and we have then to replace the 2 eqs. of hydrogen beyond it by methyle, ethyle, &c. This may be done in the case of methyle by causing bromide of methyle to act on methylamine.



Dimethylamine.—The new base is called dimethylamine. It has not yet been studied, but the corresponding ethyle base, diethylamine, has been obtained, and will be described under that head. Its formula must be $C_4 H_9 N$, and it is isomeric with ethylamine.

Hofmann has, however, obtained and described some other imide bases, in which, while the first eq. of hydrogen is replaced by methyle, the second is replaced by a different radical, such as ethyle or phenyle. Of these the best known, as yet, is Methylaniline or Methylphenylamine, $N H, Ph Me$, which is an imide base, formed from methylamine by the substitution of 1 eq. phenyle, $C_{11} H_9$, for 1 eq. of hydrogen. This base will be described under phenyle. Many similar bases will, no doubt, soon be known.

Trimethylamine.—But this is not all, for Hofmann has shown that a third series of bases, homologous with ammonia, may be obtained, in which the third eq. of hydrogen is also replaced by a radical of the methylic class, or of any other similar class. These are called *nitryle bases*, to imply that in them only the nitrogen of the ammonia is left. Ammonia may be viewed as $N + H, H, H$; and if we suppose all these eqs. of hydrogen replaced by methyle we have trimethylamine, $N + Me, Me, Me$. This base certainly exists, and has been found in the brine of pickled herrings, to which a salt of this base gives its peculiar flavor. The base, in this case, is $C_3 H_9 N$, and was at first supposed to be propylamine, $N H_2, Pr = N H_2, C_3 H_7$; but it has been shown to be really trimethylamine, which is isomeric with propylamine. Hofmann has since shown that trimethylamine and its salts possess the peculiar flavor observed in the brine above alluded to, in which trimethylamine has probably been formed by a transformation, possibly a kind of putrefaction of some animal compound contained in the fish.

The imide base, methylethylamine, $N H, Me Ae = C_4 H_9 N$, is isomeric with both trimethylamine and propylamine, but is quite distinct from both, although, like them, it is an oily base, analogous to ammonia.

As we rise higher in the series, we shall find that the number of imide and nitryle bases, isomeric with any imide base, steadily increases. The reason of this is, that, since all these classes have the same general formula $C_n H_{2n+1} N$, so when the number of eqs. of carbon increases, there must be more ways of making it up by different combinations of radicals differing by 2 eqs. of carbon, or by multiples of two. And as, for each of the three eqs. of hydrogen in ammonia, any radical of the formula $C_n H_{2n+1}$ may be substituted, all such combinations must yield $C_n H_{2n+1} N$, whatever the amount of C may be, so long as radicals of the formula $C_n H_{2n+1}$ only are used. When radicals of the phenylic series are introduced, this law no longer holds, because in that series the formula of the radicals is $C_n H_n - n$, and that of the bases formed by these radicals

must be $C_n H_n - \frac{1}{2} N$, so long as these radicals alone are used. And of course, where radicals of both series replace the hydrogen of ammonia, the formula must vary, and cannot be reduced to a general one. Ethylophenylamine, for example, which is $N H, Ae Ph$, is $= C_{16} H_{10} N$, while methylophenylamine, $N H, Me Ph$, is $C_{14} H_8 N$. These two, and others like them, would come under the formula $C_n H_n - \frac{1}{2} N$. But such a base as ethylophenylamine, $N Ae Ph$ $Ph = C_{28} H_{18} N$, and its congeners, would require the general formula $C_n H_n - \frac{1}{2} N$; and diethylophenylamine, $N, Ae Ae Ph = C_{20} H_{12} N$, would come under the general formula $C_n H_n - \frac{1}{2} N$, as would also its congeners. But the general formula $C_n H_n + \frac{1}{2} N$ will, as has been said above, include all bases, whether amide, imide, or nitrile bases, in which the hydrogen of ammonia is replaced by 1, 2, or 3 equivalents of the radicals of the methylic or ethylic series, $C_n H_n + \frac{1}{2}$. Triethylamine has been described by Hofmann.

There are many other nitrile bases, in which 2 eqs. of hydrogen are replaced by one radical, and 1 eq. by another, or all three by different radicals. Thus methylethylaniline, $N, Me, Ae, Ph = C_{18} H_{11} N$, has been obtained, with many others, by Hofmann. These will be described in their proper places.

Thus it will be seen that we are acquainted with three different forms of substitution bases, derived from ammonia, and all homologous with it. If R represent any one radical, then we have

1. Amide bases.	2. Imide bases.	3. Nitrile bases.
$N H_2 + R.$	$N H + R R.$	$N + R R R.$

And if X, Y, Z , represent any three radicals, we have

1. Amide bases.	2. Imide bases.	3. Nitrile bases.
$N H_2 + X (Y \text{ or } Z),$	$N H + X Y \text{ (or } Y Z \text{ or } X Z)$	$N + X Y Z$ or $X X Z$ or $Y Y Z, \&c.$

But even this is not all; for Hofmann, by studying the action of iodide of methyle on ammonia, has obtained a new base of the most remarkable composition and properties, which is the starting-point of a new and very extensive series of homologous compounds and substitution products.

4. *Tetramethylum*, $N, Me_4 = C_4 H_{12} N$, is obtained, in combination with iodine, when iodide of methyle acts on ammonia. Along with it, however, are formed the iodide of ammonium, and the hydriodates of methylamine, dimethylamine, and trimethylamine (which last three compounds may be also called iodides of methylum, dimethylum, and trimethylum). The new compound, like ammonium, cannot be obtained in the separate form, but its iodide crystallises; and when this salt is decomposed by oxide of silver, there is formed, along with the insoluble iodide of silver, the hydrated oxide of tetramethylum, which is soluble, and when evaporated in vacuo, yields a deliquescent crystalline mass, which, like

potash, attracts carbonic acid from the air. The oxide is a powerful base, almost caustic, and bitter. Its salts crystallise. This new base, which corresponds to hydrated oxide of ammonium, or ammonia *plus* 2 eqs. of water, $NH_3, H_2O + H_2O$, or NH_4O, H_2O , and to hydrate of potash, KO, H_2O , has all the characters of a strong alkali; whereas hydrated oxide of ammonium does not differ from ammonia and water. The new base has therefore no exact analogue. It belongs to a series quite distinct from that of methylamine, &c.; for these all correspond to ammonia, while the radical of this base corresponds to ammonium. Triethylamine, *plus* water, is a true analogue of ammonia *plus* water, but in the new base we have new characters. It is not volatile, like methylamine and its congeners, which, like ammonia, refuse to yield the oxides or hydrated oxides of their supposed metals. We should expect, from the analogy with ammonia, that on separating the hydrated oxide of tetramethylum from its salts, it would resolve itself into trimethylamine and methylic alcohol, but it does not; it forms a permanent, non-volatile hydrate. The following table shows the relations of the base to ammonia:

NH_3	= Ammonia	NMe_3	= Methylammonia (Trimethylamine)
NH_4	= Ammonium	NMe_4	= Tetramethylum
NH_4O	= Oxide of ditto	NMe_4O	= Oxide of ditto
$NH_4O + H_2O$	= Hydrated Oxide of do.	NMe_4O, H_2O	= Hydrated Oxide of ditto.

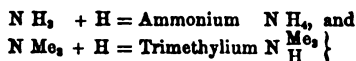
This base acts on metallic solutions like potash, and converts oils into soap when boiled with them. The chloride of tetramethylum forms with the chlorides of mercury, gold, and platinum, double salts perfectly analogous to those of potassium and ammonium. Thus,



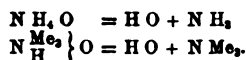
Here, then, we have a totally unexpected new series of compounds, in which the 4 eqs. of hydrogen in ammonium are all replaced by methyle and its homologues, as well as by other radicals, and in these, the supposed metals corresponding to ammonium, although not yet known in the separate state, yet yield what ammonium does not, permanent hydrated oxides. And the 4 eqs. of hydrogen may be replaced by one, by two, by three, or by four different radicals, as will be seen further on.

The best character of the hydrated oxides of these homologues of ammonium is that they are not volatile, but are decomposed by heat, and that they are powerful bases. Their existence leads to the suspicion, that there may be a base, oxide or hydrated oxide of ammonium, different from the hypothetical one, which is simply ammonia *plus* water. If such a compound exist, it will probably not be volatile without decomposition, and it may possibly be capa-

ble of assuming the separate form, under intense cold, combined with great pressure. But we must not theorise too far, nor allow ourselves to be carried away by analogy. Hitherto the fourth atom of hydrogen in ammonium, $N H_4$, or its oxide, $N H_4 O$, has been regarded as being quite distinct from the rest; when ammonia, or its salts, took up an atom of water, the hydrogen was supposed to convert the ammonia into ammonium, which then took up the oxygen to form the oxide. It was thought that trimethylamine, N, Me_3 , in which the 3 eqs. of hydrogen were replaced, was the limit of this substitution, and that we should have



and the action of trimethylamine on acids corresponds exactly to this view. It takes up 1 eq. of water, and forms, probably the oxide of trimethylum $N \begin{array}{c} Me_3 \\ H \end{array} \} O$, which, like oxide of ammonium, is resolved, when separated, into water and trimethylamine.



On this view, hydrochlorate of methylamine is chloride of trimethylum, just as hydrochlorate of ammonia is chloride of ammonium; and sulphate of trimethylamine is sulphate of oxide of trimethylum, as sulphate of ammonia is sulphate of oxide of ammonium.

But now we find that the fourth eq. of hydrogen can also be replaced by methyle, &c., and that the new metal $N Me$, is produced, which forms an oxide and a hydrate of totally new properties. Hofmann found it impossible to replace any more of the hydrogen in the new body, showing that the true limit of substitution is ammonium, $N H_4$, and not ammonia, $N H_3$. Yet when the fourth eq. of hydrogen is replaced, the base, which is now a hydrated oxide, loses the character of volatility which it had retained as long as only 3 eqs. were replaced. This proves that there is a difference, although not to the extent formerly supposed, between the fourth eq. of hydrogen in ammonium and the other three. Probably the true cause of the instability of oxide of ammonium and of those analogous compounds which like it, have 1 eq. of hydrogen, the fourth, derived from water, is this, that the tendency of their 1 eq. of oxygen to form water with 1 eq. of hydrogen is so strong as to overturn the equilibrium of the oxides; whereas, in tetramethylum, the affinity of the oxygen for the fourth atom of methyle is not sufficient to do this.

We have dwelt somewhat fully on these new compounds, not to detail their individual properties, which our space forbids, but to explain the important general laws which regulate their formation,

and which have an important bearing on the theory of the formation of natural organic bases. The reader will bear in mind that we have four series of bases derived from ammonia and ammonium; three of which are volatile like ammonia, namely, the *amide*, *imide*, and *nitryle* bases, while the fourth is not volatile without decomposition; these are called *ammonium bases*. It was necessary here to explain their nature; but we shall return to the general considerations under the head of organic bases.

Zincomethyle, $C_2 H_2, Zn$. When iodide of methyle is heated along with zinc in a sealed tube, a white crystalline product is obtained. When this product is distilled in an atmosphere of hydrogen, it yields a volatile liquid of a very fetid smell, the vapors of which are very poisonous. It takes fire spontaneously on contact with the air, and burns with a bright greenish blue flame, depositing a large quantity of zinc and oxide of zinc. This is *zincomethyle*, apparently a new radical. It was discovered by Frankland. In contact with water, it is decomposed with ignition, yielding oxide of zinc, and hyduret of methyle (marsh-gas): $C_2 H_2, Zn + H O = Zn O + (C_2 H_2, H)$

It would appear that tin, and probably also bismuth, forms a similar radical, but of these hardly any thing is yet known.

Stibiomethyle, $C_2 H_2, Sb = Sb Me_2$. This compound is formed when iodide of methyle is heated with an alloy of potassium and antimony. It is a volatile liquid of an offensive odor, spontaneously inflammable in air, insoluble in water, soluble in alcohol and ether. It is a compound radical of very powerful affinities, combining energetically with the elementary bodies. It takes up 2 eqs. of oxygen, chlorine, &c., and its oxide is basic. (Landolt.) The corresponding ethyle radical and its compounds will be described farther on.

Stibiomethylum, $C_2 H_2, Sb = Sb Me_2$. According to Landolt, when iodide of methyle is added to stibiomethyle, there is formed the crystalline iodide of a compound radical, analogous to ammonium, which he hence calls stibiomethylum. $Sb Me_2 + Me I = Sb Me_3 I$.

By the action of oxide of silver on this iodide, the oxide is formed. $Sb Me_3 I + Ag O = Ag I + Sb Me_3 O$. This is obtained as a hydrate, in the form of a white crystalline mass, $Sb Me_3 O, H O$, which in alkaline characters may be compared to caustic potash. It may be volatilised by careful heating, but if suddenly heated is decomposed, yielding vapors which take fire spontaneously. It forms, with acids, salts which are analogous to, and isomorphous with, those of oxides of potassium and ammonium.

Some very remarkable compounds are known, in which arsenic, and arsenic and platinum are combined with methyle. We shall now mention these.

When acetate of potash is heated along with arsenious acid, a

very remarkable liquid is obtained, which is the oxide of a new radical. This liquid, which is spontaneously inflammable, and has a most offensive alliaceous smell, has been long known in an impure state, under the names of the liquor of Cadet, and *alkarsine*. Bunsen, by a long series of the most profound and persevering researches, established its true character as the oxide of the radical *kakodyle*. He has even succeeded in obtaining the radical itself in the separate state, and in establishing the most perfect analogy between that radical and a metal, in all its chemical relations.

CHLOROFORM.

As *chloroform*, or the *terchloride of formyle*, has become an important anæsthetic, a few words upon its formation would not be irrelevant in this place.

This compound is best obtained by distilling pure alcohol with water and bleaching powder. The product is well washed with water and rectified, after being agitated for a short time with oil of vitriol, which removes traces of water and destroys certain oils which are usually present in small quantity. The rectified chloroform should have the Sp. Gr. 1.49 to 1.50, and should not color oil of vitriol when shaken with it, unless to a very trifling extent. If it colors the acid strongly, or if, when evaporated on the hand, it leaves an unpleasant odor, it is not fit for use, and must be again washed and rectified. It may be prepared also from pure pyroxilic spirit, but alcohol yields it purer.

Chloroform is a transparent, colorless, volatile liquid, of Sp. Gr. 1.5 : it has a peculiar heavy sweetish smell, and when inhaled from the hand, from a sponge, or handkerchief, soon produces insensibility to pain, and indeed a sort of coma. But if too sparingly or timidly applied, the effect often stops at the stage of excitement, similar to that produced by inhaling the nitrous oxide, which latter, being a gas, cannot conveniently be administered in a full dose, since one of its first effects is to relax the muscles of the mouth which grasp the tube, and thus admit air. But chloroform may be held near the mouth on a handkerchief, or a sponge, and so much given as to carry the patient beyond the stage of excitement into that of coma and entire insensibility to pain.

For the introduction of this valuable remedy we are indebted to Dr. Simpson, and although ether, benzole, and many other liquids can produce insensibility to pain, chloroform is of all the most powerful, as well as the most manageable. Of course, great care must be taken to insure its purity, for the oils which accompany it when first formed are very deleterious, and in administering it, one person should do nothing but watch the pulse and respiration of the patient, and remove the chloroform if necessary. With due precaution, chloroform is very safe; and this precaution will prevent its

being used in cases where its use is contra-indicated by disease of the heart, or by marked tendency to apoplexy. In proof of its safety, it may be mentioned that in Edinburgh, where it must now have been used in many more than 100,000 cases, no instance of a fatal result has occurred. Deaths have occurred elsewhere, but it is probable either that the chloroform was not pure, or that it was used in cases unfit for it, or finally, that due care was not taken to prevent an over-dose. That all these things can be avoided is proved by the results of the Edinburgh practice.

It has been found, of late, that although chloroform may be obtained which is quite permanent under ordinary circumstances,—for I have some which I made more than ten years ago which is still quite unaltered—yet it often, perhaps generally, happens, that exposure to the direct rays of the sun, or even to strong diffused daylight, causes a decomposition, by which chlorine is set free, the liquid becomes yellowish, and it acquires of course the suffocating smell of chlorine, so that it cannot be used for inhalation. It is probable that this depends on the purity of the chloroform, for I have found that those portions which I had purified with the greatest care were the soonest decomposed by sunlight. It may, however, also depend on the presence of traces of substances used in purifying it, which may promote decomposition; though, in the case of prussic acid, we find that a trace of sulphuric ether has the effect of rendering it more permanent.

This point is not yet cleared up, but, however it may be, it is easy to preserve chloroform unchanged, by keeping it in a rather dark place, or by storing it, either in bottles of dark-colored glass, or in bottles covered with dark paper. Even in clear glass, however, it usually keeps well in the ordinary light of a room into which the sun does not directly shine.

It has been doubted whether the protoxide of nitrogen can produce insensibility to pain, and whether its action resembles that of chloroform. I can only state, that I have seen many cases among those who have inhaled the gas, where insensibility to pain was perfectly developed. This has occurred, not only in such as were rendered apparently insensible to all surrounding objects for a short time, which is now and then seen, but also in several who were, while under the influence of the gas, violently excited and prone to laughter and muscular exertion. Some of these have struck wood or stone with their hands, till these were covered with blood, and have not even known this, till the effect passed off, not having felt any inducement to look at their hands. But I have also tested the insensibility to pain in various ways.

In some cases, as already hinted, there was produced the same half comatose state as is produced by a full dose of chloroform. These were very sensitive subjects, who had got a full dose of the gas before the muscles of their lips relaxed. But such cases are rare.

On the other hand, chloroform, in insufficient quantity to cause the coma, often produces laughter, singing, and violent muscular efforts, exactly like the gas; and when to this we add that the taste of the gas is almost the same as that of chloroform, and that it produces the very same thrilling warmth over the whole system as chloroform and ether do, as I can testify from personal experience, it appears reasonable to conclude that their action is alike, and that the differences observed are only those of an earlier or a later stage of that action, the former being the rule in the case of the gas, from the mechanical causes I have specified, the latter being the rule in the case of chloroform or ether, of which a full dose is easily administered.

When acted on by chlorine, perchloride of formyle yields perchloride of carbon, $C_4 Cl_4 = C_2 Cl Cl_3$, just as perchloride of acetylene, $C_4 H_2 Cl_4$, yields sesquichloride of carbon, $C_4 Cl_4 = C_2 Cl_3, Cl_2$.

There are several combinations of ethyle with the metals, phosphorus, &c., which have been discovered quite lately, and which it is important the student should be acquainted with. For instance:

Zyncethyle, $C_4 H_4 Zn = Ae Zn$. This compound is obtained by distilling the crystalline product formed by the action of zinc on iodide of ethyle (Frankland). It is a volatile, fetid, poisonous, and highly inflammable liquid, and like zincmethyle, appears to be an electro-positive radical, although its compounds have not yet been examined minutely. In contact with water, it is decomposed, yielding oxide of zinc and a carbo-hydrogen of the formula $C_4 H_4 + 1$. Thus $C_4 H_4 Zn + H O = Zn O + C_4 H_4$. This body, $C_4 H_4$, is most probably hyduret of ethyle, $C_4 H_4, H$, or $Ae H$. But it may also be the radical methyle, for $C_4 H_4 = 2 (C_2 H_2)$. The latter view, however, has been shown by Frankland to be less probable, and we shall consider the body $C_4 H_4$ as the hyduret of ethyle, while the compound $C_4 H_4$, or the radical methyle, polymeric with it, is that formed in the electrolytic decomposition of acetic acid.

Stibethyle, $Sb C_4 H_4 = Sb Ae, = Sbæ$. This radical is obtained when the alloy of antimony and potassium is heated with iodide of ethyle. It is a very mobile, highly refracting liquid, of an offensive alliaceous odor, which, when exposed to the air, first forms a thick white smoke, and then takes fire, burning with a very luminous white flame. It boils at 302° , and its Sp. G. is 1.324, that of its vapor 7.499. It is heavier than water, and soluble in alcohol or ether. When it is slowly oxidised, it yields two compounds. The first is a viscid transparent body, and is an oxide of stibethyle, $Sb Ae_2, O_2 = Sbæ O_2$. The other is a compound of antimonious acid with oxide of stibethyle. This compound does not crystallise, and its solutions when warmed become thick and gelatinous, and dry up into a friable porcelain-like mass. It has a very bitter taste, and gives, with sulphuretted hydrogen, a light yellow precipitate.

The oxide of the radical, stibethyle, forms with acids crystalline-

ble salts. Both the oxide and its salts are very bitter. The nitrate forms fine large rhombohedral crystals, very soluble in water. Its formula is $\text{Sb Ae, O}_6, 2 \text{ N O} = \text{Sbæ O}_6, 2 \text{ N O}_2$. The sulphate is $\text{Sb Ae, O}_6, 2 \text{ S O}_3 = \text{Sbæ O}_6, 2 \text{ S O}_4$.

Sulphide of Stibethyle, Sbæ S_2 , forms small white crystals, of a brilliant silvery lustre, alliaceous smell, and bitter, hepatic taste. It is soluble in water, and precipitates metallic solutions, like sulphide of potassium. The selenide, Sbæ Se_2 , resembles the sulphide. The iodide, Sbæ I_2 , crystallises beautifully. It is fusible, and in its reactions resembles iodide of potassium. Bromide of stibethyle, Sbæ Br_2 , is a transparent liquid, of Sp. G. 1.953, which crystallises when exposed to cold. The chloride is a liquid of Sp. G. 1.54. All these compounds exhibit the reaction of metallic salts, chlorides, bromides, &c.

Stibethyle is remarkable for its very strong affinities. In fact, it combines directly with almost all the non-metallic elements, and with so much energy, that it generally takes fire, and it is therefore necessary to employ indirect or slow methods of forming its compounds. Its affinities are almost, if not quite, as powerful as those of potassium. Löwig and Schweizer, who discovered it, are of opinion that it is a coupled radical, of the formula Sb Ae, Ae_2 , and that this is the reason why it combines with 2 eqs. of oxygen, sulphur, &c.; its affinities depending on the 2 eqs. of ethyle, and not on the copula Sb Ae .

Stibethylium, $\text{Sb Ae,} = \text{C}_{16} \text{ H}_{20} \text{ Sb}$. This compound metal, corresponding to ammonium, and having antimony instead of nitrogen, and ethyle instead of hydrogen, is analogous to stibio-methylum. It is unknown in the separate form, but its iodide is obtained by the action of iodide of ethyle on stibethyle. This oxide, being acted on by oxide of silver, yields the hydrated oxide of stibethylium, analogous to caustic potash. It has not been yet fully studied.

Bismethyles. There are two compounds of bismuth with ethyle. Bismotriethyle, $\text{C}_{18} \text{ H}_4 \text{ Bi}$, is formed when iodide of ethyle acts on an alloy of bismuth and potassium. It cannot be distilled, and is purified by solution in ether, adding water, and distilling off the ether in close vessels filled with carbonic acid gas. The new radical remains under the water as a yellow oil, very easily decomposed, both by air and moisture. Its density is 1.82, and it ferments in the air, taking fire after a short exposure. Its taste and smell are unpleasant. When heated, it is decomposed, and at a certain point it explodes with violence. Its compounds with chlorine, iodine, &c., are very unstable.

When it is acted on by the bichloride of mercury, there are formed chloride of mercurethyle, and chloride of a new radical bismethyle, C, H, Bi . The iodide of this radical forms very fine hexagonal crystals. The other compounds are unstable.

Stannethyle, $\text{Sn Ae} = \text{C}_4 \text{H}_4 \text{Sn}$, is analogous to zincethyle, and is obtained in the same way.

It forms an oxide, Sn Ae O , which is a bulky, insoluble, white powder. The chloride, bromide, and iodide all crystallise easily, and are more or less soluble in water. The nitrate of the oxide also crystallises. The other salts are generally insoluble, as is also the sulphide.

Löwig states, that there exist besides stannethyle, several other compounds, such as $\text{Sn}_2 \text{ Ae}_2$, $\text{Sn}_4 \text{ Ae}_4$, $\text{Sn}_4 \text{ Ae}_6$, $\text{Sn}_4 \text{ Ae}_8$, $\text{Sn}_4 \text{ Ae}_{10}$, $\text{Sn}_4 \text{ Ae}_{12}$, all of which, like stannethyle, are compound metals in their chemical relations. They form oxides, chlorides, bromides, iodides, &c., many, if not all of which, as well as the salts of the oxides, crystallise well.

It will be observed, that some of these formulæ are multiples of that of stannethyle. These, as well as the other formulæ, are strange, and it is probable that these compounds are not yet fully understood.

Arsenodiethyle, $\text{Ae}_2 \text{ As}$, is homologous with cacodyle or Arsenobimethyle, $\text{Me}_2 \text{ As}$. It is formed when arsenic acts on iodide of ethyle, and is obtained as an iodide, $\text{Ae}_2 \text{ As I}$. It resembles cacodyle in all its characters and relations.

Arsenethyle $\text{Ae}_2 \text{ As}$, is formed along with the preceding, and is analogous to stibethyle. It is also a volatile fetid liquid. Its oxide is an oily liquid, its sulphide is crystallisable. The chloride is not known in a separate form, but is volatile and attacks the eyes violently. The iodide forms yellow flocks, easily decomposed.

Arsenethylum, $\text{Ae}_4 \text{ As}$ or As Ae_4 , analogous to ammonium and stibethylum, is formed by the action of iodide of ethyle on arsenethyle, as an iodide. The hydrated oxide is a strong base, the chloride and iodide are crystalline.

Plumbethyle, $\text{Pb}_2 \text{ Ae}_2$, is obtained as iodide, when iodide of ethyle acts on an alloy of sodium and lead. There appear to be several compounds of lead with ethyle, but the one above named is a volatile liquid, insoluble in water. It is oxidised by exposure to air. The hydrated oxide is a strong base, which crystallises. Its formula is not fixed, but as it is caustic, attracts carbonic acid from the air, and in other respects resembles caustic potash, and as the chloride and bromide contain only 1 eq. of salt radical, it is probably $(\text{Pb}_2 \text{ Ae}_2) \text{ O}$, H O . The chloride and bromide crystallise, as do the sulphate, nitrate, and carbonate of the oxide.

Mercurethyle, $\text{Hg}_2 \text{ Ae}_2$, is formed when iodide of ethyle acts on mercury. The hydrated oxide, probably $\text{Hg}_2 \text{ Ae O}$, H O , is a powerful caustic base, like caustic potash. The chloride, bromide, and iodide crystallise.

Tellurethyle, $\text{C}_4 \text{ H}_4 \text{ Te} = \text{Te Ae}$. This radical is obtained when sulphovinate of baryta is distilled with telluret of sodium (Wöhler). It is a deep red liquid, heavier than water, in which it is sparingly

soluble. It has a very offensive smell, and is poisonous. Its oxide, Te Ae O , is a crystallisable base, forming salts with acids. Its chloride, Te Ae Cl , is a colorless liquid, of a disagreeable odor, volatile without decomposition.

Mallet, who has ascertained the true nature of tellurethyle, has also obtained another compound, which is either bitelluret of ethyle, Ae Te_2 , and probably also a radical, or else a compound analogous to mercaptan, $\text{C}_2\text{H}_5\text{Te}$, H Te , which only differs from the other by 1 eq. hydrogen. It is a very offensive liquid.

Thénard has also indicated the existence of compounds of phosphorus and ethyle, corresponding to those described under methyle, but has not yet described them. It is evident that an immense number of new compounds, containing metals, phosphorus, and other elements, along with organic groups, and having, like those here described, very remarkable properties, must very soon be discovered.

There are several salts of the oxide of ethyle which are important, and which have been discovered and studied since the last edition of this work. For instance:

Perchlorate of Oxide of Ethyle, $\text{C}_2\text{H}_5\text{O, Cl O, = Ae O, Oe O}$. *Syn. Perchloric Ether*. This ether is prepared by distilling a mixture of 1 part of perchlorate of baryta with one part of crystallised ethylsulphate (sulphovisate) of baryta. The mixture must be in a small retort, and must not exceed 1 drachm in weight; and it is heated gradually in an oil bath. A U-shaped tube serves as receiver, and is kept cold by a freezing mixture. Up to 212° , and as long as the water of crystallisation has not been expelled, no explosion need be feared. The retort is then gently heated to not beyond 340°F ., at which point the action is completed. In the receiver is found the new ether, under a stratum of water; the latter is removed cautiously, by means of slips of bibulous paper, without touching the receiver with the hand, because a slight motion may cause explosion.

Perchloric ether is a liquid heavier than water, and insoluble in it, of an agreeable odor, and a taste at first sweet, then pungent, like cinnamon. It neither boils nor explodes when heated to 212° with care. But a stronger heat or friction, or percussion, will cause it to explode, which it does with greater violence than any known compound. It is very apt to explode from causes so slight that it appears to do so without any cause, and is therefore extremely dangerous. In making and experimenting on it, the operator must be protected by very thick gloves, and a strong mask with thick glass eye-holes.

This dangerous compound can only be kept safely when it is mixed with a sufficient quantity of absolute alcohol, which dissolves it.

A little of this solution, on the addition of water, deposits the

ether, which collects below in a drop of size proportioned to the quantity employed. If the water be decanted off with care, and the last portion of it taken up by paper, the drop of ether may be made to detonate on a plate or capsule, by touching it with a hot body, or by a slight blow with a hammer. The smallest drop inevitably shatters the vessel on which it rests.

The cause of the explosion is evidently twofold. First, the compound is unstable, from its complexity, its empirical formula being $C_2 H_4 Cl O_2$. Secondly, the hydrogen has a very strong affinity both for oxygen and chlorine, and the carbon for oxygen, and there is oxygen enough present to convert the whole into gaseous compounds.

For $C_2 H_4 Cl O_2 = H Cl + 4 H O + 4 C O$, so that it is entirely resolved into hydrochloric acid, steam, and carbonic oxide gas; and as this takes place instantaneously, much heat is developed, which heats and expands to a high degree the gases formed.

Borates of Oxide of Ethyle.—There appear to be several borates of oxide of ethyle, or boracic ethers. The neutral borate is $3 Ae O + B O_3$, corresponding to a terhydrate of the acid, $3 H O + B O_3$. It is obtained by the action of chloride of boron on absolute alcohol, and is a mobile liquid of a peculiar pleasant odor, and a warm bitter taste. Its density is 0.8849; that of its gas is 5.14, corresponding to 4 vols. for the formula above given. It boils at $248^\circ F.$, and is decomposed by water, which dissolves it, yielding boracic acid and alcohol.

Another borate is the biborate of ethyle, $Ae O, 2 B O_3$; which is formed by the action of boracic acid, previously fused to expel all water, on absolute alcohol. It is a viscid liquid of an ethereal smell and a pungent taste.

Silicates of Oxide of Ethyle.—These are also several silicic ethers. That formed by the action of chloride of silicon on absolute alcohol, is $4 Ae O + 4 Si O$. It is a limpid ether, of a pleasant odor and pungent taste, of Sp. G. 0.933 at $68^\circ F.$, insoluble in water, which gradually decomposes it. It boils at about $330^\circ F.$, and the density of its gas is $7.32 = 4$ vols. for the above formula.

There are two other compounds, the bisilicate, $Ae O, 2 Si O$, and the quadrisilicate, $Ae O, 4 Si O$. The former is a liquid of Sp. G. 1.079, boiling at $662^\circ F.$ When left in contact with water, it is slowly decomposed, and the silicic acid is deposited as a hydrate, which is transparent and glassy, but contracts ultimately to a mass of hyaline quartz, sufficiently hard to scratch glass, and which in some cases is true hydrophane; that is, like that mineral, it becomes transparent in water.

The quadrisilicate is a glassy mass, like amber, softening by heat, and when still more strongly heated, yielding silicic acid, and the first ether or protosilicate. It is soluble in alcohol, ether, and the two preceding ethers.

Chlorocarbonic Ether, $C_2 H_5 Cl O_2 = C_2 H_5 O + C_2 \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\}$ is formed when absolute alcohol is placed in contact with chlorocarbonic acid gas. It appears as an oily liquid, of Sp. G. 1.133, boiling at 200° . It is formed as follows: 2 eqs. of chlorocarbonic acid and 1 of alcohol, losing 1 eq. hydrochloric acid, yield 1 eq. of the new ether. $C_2 O_2 Cl_2 + C_2 H_5 O_2 = H Cl + C_2 H_5 Cl O_2$. It may be viewed as a compound of oxide of ethyle, with a peculiar acid, $C_2 \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\}$; or as carbonic ether, $C_2 H_5 O_2$, plus 1 eq. chlorocarbonic acid, $C \left\{ \begin{smallmatrix} O \\ Cl \end{smallmatrix} \right\}$.

Carbamate of Oxide of Ethyle, Carbamic Ether, $C_2 H_5 N O_2$. SYN. *Urethane*, is formed by the action of ammonia on the preceding compound, along with sal-ammoniac, from which it is separated by being sublimed, or rather distilled, when it passes over at a gentle heat, as a liquid which crystallises on cooling. It is very soluble in water and alcohol, and yields very large crystals. It may be viewed as chlorocarbonic ether, in which amide, $N H_2$, has been substituted for the chlorine, $C_2 H_5 O + C_2 \left\{ \begin{smallmatrix} O_2 \\ N H_2 \end{smallmatrix} \right\}$. It is formed as follows: $C_2 H_5 Cl O_2 + 2 N H_3 = (N H_2, H Cl) + C_2 H_5 N O_2$. Berzelius, with much probability, considers it as a compound of oxide of ethyle with an acid, not yet known in the separate form, containing the elements of carbonic acid and carbamide, just as oxamic acid does those of oxalic acid and oxamide. On this view its rational formula will be $C_2 H_5 O + C O_2, C O N H_2 = C_2 N H_5 O_2$.

Oxide of Ethyle.

Carbamic Acid.

It is remarkable that three other compounds, quite distinct in properties, have the same empirical formula as urethane or carbamic ether. These are *lactamide*, or anhydrous lactate of ammonia, $C_3 H_5 O_2 + N H_3$; *sarcosine*, $C_3 N H_7 O_2$, a new base, derived from creatine, and *alanine*, a compound homologous with glycocine.

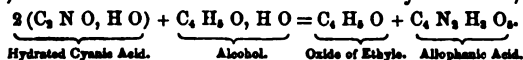
Cyanate of Oxide of Ethyle. SYN. *Cyanic Ether*. $Ac O, Cy O = C_2 N H_5 O_2$. Obtained by Wurtz by heating sulphovinate with cyanate of potash. It is a very pungent, volatile liquid. The Sp. G. of its vapor is 2.4. It forms, with ammonia, a crystalline body, $C_2 N_2 H_5 O_2 = N H_3 + C_2 N H_5 O_2$. The constitution of this compound is uncertain. In contact with water, cyanic ether yields carbonic acid and a new compound, $2 (C_2 N H_5 O_2) + 2 H O = 2 C O_2 + C_{10} N_2 H_{12} O_2$. The latter body is crystalline, soluble in alcohol and water. It is either butylo-urea (a body homologous with urea), or diethylo-urea, which is isomeric with that compound.

Ethylo-urea, $C_2 N_2 H_5 O_2$, is formed when cyanate of potash is heated in solution with sulphate of ethylamine. The substance

thus formed is truly homologous with urea and methylo-urea. Its formation corresponds to that of urea from cyanate of potash and sulphate of ammonia, $K O, C_2 N O + C_4 H_7 N, H O, S O_3 = K O, S O_3 + C_6 N_2 H_8 O_2$.

Allophanate of Oxide of Ethyle.—This compound is formed when the vapor of hydrated cyanic acid is brought in contact with a mixture of ether and alcohol. It forms brilliant prisms, which may be purified from cyamelide by being dissolved in boiling alcohol, or in boiling water. Its formula is $C_4 N_2 H_8 O_6 = C_4 H_8 O, C_4 N_2 H_8 O_5$. It was formerly supposed to consist of 2 eqs. hydrated cyanuric acid, 3 eqs. oxide of ethyle, and 3 eqs. of water; and it is, in fact, resolved by heat into alcohol and cyanuric acid. But Liebig and Wöhler have shown that it is composed of oxide of ethyle and of a new acid, namely, anhydrous allophanic acid, $C_4 N_2 H_8 O_5$. The former view was quite anomalous, since oxide of ethyle unites only with anhydrous acids; and the latter, therefore, brings the compound into the ordinary category of compound ethers.

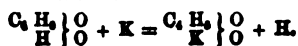
Allophanic acid is unknown in the hydrated or separate state, the formula of which would be $C_4 N_2 H_8 O_5, H O = C_4 N_2 H_8 O_6$. It forms crystallisable salts with baryta, potash, and soda, but when we attempt to isolate it, it is resolved into urea and carbonic acid, $C_4 N_2 H_8 O_6 = C_2 N_2 H_4 O_3 + 2 C O_2$. Allophanic acid is produced by the action of 2 eqs. of hydrated cyanic acid on 1 eq. of alcohol. The water of the alcohol, added to the cyanic acid, produces the new acid, which combines with the oxide of ethyle. Thus,



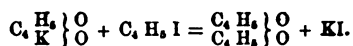
Cyanurate of Oxide of Ethyle. $Cy, O_3, 3 Ae O = C_{15} N_3 H_{15} O_6$ (Wurtz). *Syn. Cyanuric Ether.* This compound is obtained by heating sulphovinate of potash with tribasic cyanurate of potash. It forms brilliant crystals, melting at 185° , and boils at about 529° . The density of its vapor is 7.4. It is soluble in alcohol and ether.

Limpricht has discovered a compound, $C_{14} N_2 H_{11} O_6$, which may be viewed as a cyanuric ether, with 2 eqs. of oxide of ethyle and one of basic water, $C_6 N_2 O_3 + 2 Ae O \left\{ \begin{array}{l} O \\ H O \end{array} \right\}$. But he is of opinion that neither this nor the preceding compound are true ethers, because they do not yield cyanuric acid and alcohol when heated with potash, but carbonic acid and ethylamine. If not true cyanuric ethers, they are at least isomeric with such compounds.

Oxide of Ethyle and Potassium. $C_4 H_8 O, KO = \begin{array}{c} C_4 H_8 \{ O \\ K \} O \end{array}$. *Syn. Alcoholate of Potash.* This body is formed when potassium acts on pure anhydrous alcohol:

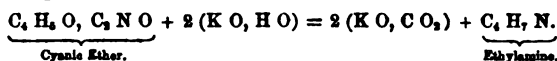


It forms large transparent crystals. When acted on by chloride or iodide of ethyle, oxide of ethyle is reproduced, thus :

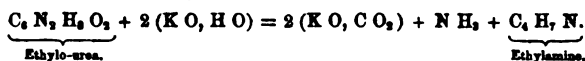


BASES CONTAINING ETHYLE.

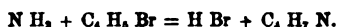
Ethylamine, $\text{C}_2 \text{H}_5 \text{N} = \text{N H}_2$ Ae. This base, discovered by Wurtz, is homologous with methylamine, and is obtained exactly in the same way, by heating cyanic ether, cyanuric ether, or ethylurea with potash.



We have only to treble this equation to explain the formation of ethylamine from cyanuric ether. The following equation explains its production from ethylurea.



Ethylamine may be obtained by other processes. Hofmann has produced it by the action of bromide of ethyle on ammonia.



Strecker has discovered another method of obtaining it. When neutral sulphate of oxide of ethyle is acted on by dry ammonia, there is formed the ammonia salt of a new acid, sulphethamic acid. When this salt is boiled with carbonate of baryta till all ammonia is expelled, and the residue distilled with potash, ethylamine is obtained. The sulphethamic acid ($\text{C}_{16} \text{N H}_{22} \text{O}_4, 4 \text{S O}_3$) yields, when decomposed, several different products, and as all of these are not yet known, the change cannot be represented in the form of an equation.

Lastly, ethylamine is found in the basic oil of coal-tar, and in the basic part of animal oil, produced by the distillation of animal matter; and it appears also to occur among the products of the oxidation of some vegetable products. At all events, other bases of this series, such as methylamine, propylamine, and butylamine, are so produced. It is probable that many sources of ethylamine remain to be discovered.

Ethylamine is a volatile liquid, boiling at 68°F . Its density in the liquid form is 0.6964 at 45°F . The density of its gas is 1.57 to 1.60. The density of its vapor is 1.5568. It mixes readily with water, developing heat. It has a very pungent ammoniacal smell, with something putrid or empyreumatic. This is natural, since the smell of empyreumatic animal oil is made up of those of ammonia, methylamine, ethylamine, &c., besides other oils, such as creosote.

It is also probable that in the putrefaction of animal matter, not only ammonia, but also methylamine and ethylamine, are formed. Ethylamine has no doubt long been overlooked from its great resemblance to ammonia. It is powerfully rubefacient, and even caustic. It takes fire on the contact of a light, and burns with a yellowish flame.

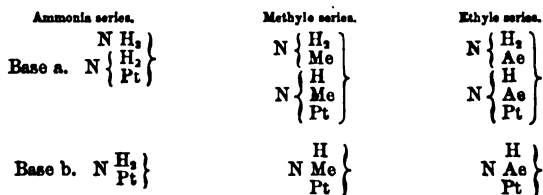
It is a very strong base, being the second in the series of methylamine. Its rational formula is Ad Ae , or $\text{N H}_2 \text{ Ae}$, which may be thus compared to ammonia, Ad H , or N H_2 , H.



Like methylamine, it is an amide base of the general formula $\text{N H}_2 + \text{R}$, or Ad R ; R being hydrogen, or any radical of the methyle series, or even of other series, such as that of phenyle. It expels ammonia from its salts, with the aid of heat, and acts on metallic solutions very much as ammonia and methylamine do. An excess of it dissolves alumina even more readily than ammonia does.

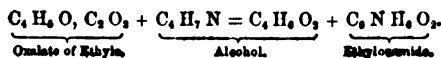
The salts of ethylamine resemble those of ammonia and methylamine. It forms double chlorides with the chlorides of mercury, gold, and platinum. The latter salt forms golden-yellow crystals, more soluble than the corresponding compound of ammonia.

Ethylamine acts like ammonia and methylamine on the protochloride of platinum, and gives rise to two new platinised bases, probably to as many as ammonia. Wurtz compares as follows the two bases of Reiset with their homologues containing ethylamine and methylamine:



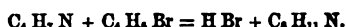
It cannot be doubted that all the other platinised bases will also find homologues in the ethyle and methyle series; and farther, that similar compounds may be formed with the other members of the series, homologous with methyle and ethyle.

When ethylamine is acted on by oxalic ether, there is formed *ethylloxamide*, homologous with oxamide. Its formula is $\text{C}_4 \text{ N H}_2 \text{ O}_2$. It is soluble and crystallisable, and represents oxamide, in which 1 eq. of hydrogen is replaced by ethyle. Its formation is as follows:



The acid amide, corresponding to oxamic acid, probably exists, but has not yet been described, as in the case of methylamine it has.

Diethylamine, $C_2 H_5 N = N H, Ae_2$. This is an imide base; that is, ammonia, in which 2 eqs. of hydrogen are replaced by ethyle. It is formed by the action of bromide of ethyle on ethylamine, thus:



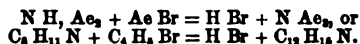
It is a volatile inflammable oil, soluble in water, and strongly basic. Its salts have been little examined.

If bromide of ethyle were made to act on methylamine, or bromide of methyle on ethylamine, it is quite certain that the result would be the formation of an imide base, ethylomethylamine or methylethylamine, $C_2 H_5 N$, in which the 2 eqs. of hydrogen are replaced by two different radicals.



We shall see further on that several similar imide bases have thus been formed.

Triethylamine, $C_3 H_7 N = N Ae_3$. This is a nitryle base, or ammonia, in which all 3 eqs. of hydrogen are replaced by ethyle. It is obtained by the action of bromide of ethyle on diethylamine, thus:



It is a light, volatile, inflammable liquid, but less so than diethylamine, and it has strong basic properties. The double chloride of triethylamine and platinum is very soluble, and forms large and fine aurora-red crystals.

It is evident that we may expect to obtain other nitryle bases, in which both methyle and ethyle are present, such as diethylomethylamine, $N, Me Ae_2$, and dimethylethylamine, $N, Me_2 Ae$. But these, as well as trimethylamine, $N Me_3$, are not yet known. We shall find that various nitryle bases, however, are already known, in which ethyle is associated with other radicals to be afterwards described—namely, amyle, $C_{10} H_{21}$, and phenyle, $C_{11} H_7$.

The three ethyle bases above described, ethylamine, diethylamine, and triethylamine, are all formed when bromide of ethyle acts on ammonia. In them the 3 eqs. of hydrogen are successively replaced by ethyle, while the type of ammonia remains entire; for all these bases are volatile, and in the highest degree analogous to ammonia. But the action does not stop here, for a fourth compound is formed, along with the three preceding, and in this, as we have seen under methyle, the type is changed, the base is no longer volatile, but its basic properties are stronger than ever.

Tetrethylum, $N Ae_4$, is formed along with the three preceding

bases, in the action of bromide of ethyle on ammonia, or still better, when triethylamine is acted on by iodide of ethyle.



The compound $N Ae_4 I$ is the iodide of tetrethylum, and when this is decomposed by oxide of silver, iodide of silver and oxide of tetrethylum are formed. $N Ae_4 I + Ag O = Ag I + N Ae_4 O$. The oxide dissolves in water, and by evaporation is obtained as a caustic hydrate in crystals, which, like caustic potash, absorb water and carbonic acid from the air. The group $N Ae_4 = C_{16} H_{20} N$, is really in its chemical relations an organic metal, perfectly analogous to ammonium and to potassium. The oxide resembles potash, and has at once the caustic taste of that alkali and the bitterness of quinine. It saponifies the oils just as potash does, and in all its reactions, on metallic solutions as well as on organic compounds, it closely resembles potash.

Under the corresponding methyle compound, the analogies and the differences between that compound and its oxide on the one hand, and ammonium and its oxide on the other, have been fully pointed out.

When heated, the hydrated oxide is resolved into triethylamine, water, and olefant gas, $N Ae_4 O, H O = N Ae_3 + 2 H O + C_2 H_4$.

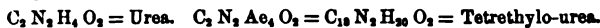
The salts of this base are crystallisable, but most of them are deliquescent. The double chloride of tetrethylum and platinum, $N Ae_4 Cl_2, Pt Cl_2$, instead of being more soluble than the corresponding salt of triethylamine, is, like those of potassium and ammonium, sparingly soluble.

Methylotriethylum, $C_{14} H_{18} M = N Me Ae_3$, is formed when iodide of methyle acts on triethylamine. It corresponds in characters to tetrethylum, and its oxide is a powerful bitter base, yielding crystallisable salts with acids. It is decomposed by heat, but the products have not been studied. It will, no doubt, yield water, a carbo-hydrogen, and either triethylamine or methylodiethylamine.

The four ethylised bases, when acted on by chlorine and bromine, yield substitution products, in which, however, the basic character is lost. This evidently because the chlorine or bromine introduced does not replace the basic hydrogen of ammonia, but some of the hydrogen of the ethyle. Wurtz has described dichlorethylamine, $C_4 H_9 Cl, N = N H_2, C_2 H_5 \left\{ \begin{smallmatrix} H \\ Cl \end{smallmatrix} \right\}$, and dibromethylamine, $N H_2, C_2 H_5 \left\{ \begin{smallmatrix} H \\ Br \end{smallmatrix} \right\}$. Hofmann has obtained corresponding substitution products from tetrethylum, in which the hydrogen is partially replaced by chlorine, bromine, and iodine; they crystallise beautifully, but are not basic.

According to Hofmann, when cyanic acid is added to the hydrated oxide of tetrethylum, there is obtained a crystalline body,

which is an urea, in which the four eqs. of hydrogen are replaced by 4 eqs. of ethyle.



We have thus seen that ethylised compounds exist, all of which are basic, but which belong to four different classes of bases; three of these, the amide, imide, and nitryle bases, being volatile homologues of ammonia, and the fourth, or ammonium bases, homologues of oxide of ammonium, but differing from it in this, that while ammonium is resolved into ammonia and hydrogen, and oxide of ammonium seems to be identical with ammonia *plus* water, these ammonium bases have acquired new and permanent characters, ceasing to be volatile without decomposition, and exactly resembling oxide of potassium.

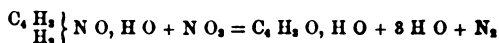
A number of new compounds of acetyls have lately been discovered, some of which are bases. The following are among the principal ones:

Acetylammonium.—Natanson has recently shown that acetyls, $C_2 H_3$, is capable of replacing 1 eq. of hydrogen in ammonium, $N H_4$, yielding a new radical or compound metal, acetylammonium. $N \begin{smallmatrix} H_3 \\ C_2 H_3 \end{smallmatrix} \} = C_2 H_3 N$. This is unknown in the separate state, but its hydrated oxide is a base.

Hydrated Oxide of Acetylammonium, $C_2 H_3 N O, H O$, is best obtained from the oil of olefant gas, $C_2 H_3 Cl$. When this oil, which is the hydrochlorate of the chloride of acetyls, $C_2 H_3 Cl, H Cl$, is heated 302° in a sealed tube, with five times its bulk of the strongest aqua ammonia, it is dissolved and a yellow liquid obtained, which contains sal ammoniac and the chloride of the new radical, $C_2 H_3 Cl, H Cl + 2 N H_3 = N H_4 Cl + N \begin{smallmatrix} H_3 \\ C_2 H_3 \end{smallmatrix} \} Cl$.

After the sal ammoniac has been separated by crystallisation, the mother liquid, which contains the chloride of acetylammonium, is acted on by moist oxide of silver, evaporated to dryness to expel the excess of ammonia; the residue, dissolved in water, treated with sulphuretted hydrogen to remove some silver dissolved by the new base, and the filtered liquid is now a solution of the hydrated oxide of acetylammonium. It is carefully neutralised by sulphuric acid the sulphate decomposed by baryta water, taking care to avoid excess of baryta, and from the mass alcohol dissolves the new base.

Neither the hydrated oxide, nor its salts can be obtained in crystals, but their constitution is demonstrated by their reactions. Thus, when to the solution of oxide, hyponitrite of silver is added, with a little sulphuric acid, and heat applied, aldehyde is regenerated.



This exactly corresponds to the action of hyponitrous acid on

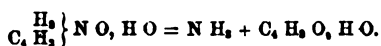
ethylamine, when alcohol is regenerated, and proves that the new compound contains acetylene replacing hydrogen.

With nitrate of silver and ammonia, the base or its salts yield a mirror-like deposit of silver, proving that here also aldehyde, that is, hydrated oxide of acetylene, is regenerated.

The hydrated oxide, when its solution is dried up, forms a tough yellow amorphous mass. Its solution has a strong alkaline reaction, and a feeble caustic taste. When boiled, it has the peculiar odor of alkaline leys. The new base expels ammonia from its salts and attracts carbonic acid from the air. It is, therefore, like the hydrated oxide of tetraethylum, analogous in constitution to hydrated oxide of ammonium, and in properties, to hydrated oxide of potassium or caustic potash. It is, however, from the negative character of acetylene, a weak base, and its salts, with the stronger acids, are all somewhat acid.

These researches of Natanson are not yet completed, but we have given here the first part of them, because they have an important bearing on the question of the real existence of the negative radicals, formyle, acetylene, and their homologues. It is evident that the existence of the base just described, is strongly in favor of the view which admits these radicals. We may expect, not only that many bases, homologous with this one, and containing radicals higher in the scale, will be obtained, but also that similar compounds may be formed, in which two, three, or all four of the equivalents of hydrogen in ammonium are replaced by formyle, acetylene, &c., or partly by one and partly by another of these radicals, or even partly by these, and partly by ethylic or phenylic radicals.

It might be expected that as hydrated oxide of tetraethylum, when heated, yields triethylamine and alcohol, $N Ae, O, H O = N Ae, + Ae O, H O$, the hydrated oxide of acetylammmonium should yield ammonia and aldehyde when heated,



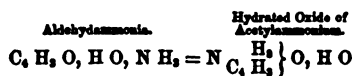
This, perhaps, takes place, but at the same time the base is charred, so that a further decomposition cannot be avoided.

Natanson has not yet been able to obtain any *volatile bases* analogous to ethylamine, &c., containing acetylene, as replacing the hydrogen of ammonia. And from the circumstances that in the action of ammonia on the oil of olefiant gas, we obtain, not hydrochlorate of acetylamine, $N \left. \begin{matrix} H_2 \\ C, H_2 \end{matrix} \right\}, H Cl$, but chloride of acetylammmonium,

$N \left. \begin{matrix} H_2 \\ C, H_2 \end{matrix} \right\} Cl$, he draws the conclusion that the true fundamental bases are the ammonium bases, such as oxide of ammonium, or of tetraethylum, and that the volatile or ammonia bases are merely products of their decomposition. He infers also, that the ammo-

num theory of ammoniacal compounds is the only true one. But it is not easy to see how the facts prove these inferences; for oxide of ammonium is unknown in the free state, and his own base does not yield, when heated, the products which we should anticipate. It would seem rather that something in the relations of nitrogen and hydrogen renders ammonia, $N H_3$, as well as its numerous homologues, very permanent: while oxide, or hydrated oxide of ammonium, $N H_4 O$, $H O$, is so unstable as not to be known in the free state, on account of the attraction of oxygen for the fourth eq. of hydrogen. In the ammonium bases, the fourth eq. being ethyle, methyle, acetyle, or other similar radicals, has no such strong tendency to combine with oxygen, and therefore the compound molecule is more permanent.

It is worthy of remark, that hydrated oxide of acetylammonium is isomeric with aldehydammonia; for,



the empirical formula of both being $C_2 H_7 N O_2$. The differences in their properties are accounted for by the rational formulæ above given, while the fact that they agree in some points, as in reducing the salts of silver, is also accounted for by both containing acetyle, and yielding aldehyde when decomposed.

The Benzole Compounds.—Some of these compounds will be found at page 347, but since the last edition of this work, not only several new ones have been discovered, but the new series of compounds, homologous with benzole, has been studied more comprehensively. This substance is the starting-point of a series of homologous compounds, the general formula of which is $C_n H_n$ —, and the common difference added at each step, is $C_2 H_2$. These compounds are all fragrant aromatic volatile oily liquids, or as we rise in the scale, fusible solids. They all admit of their hydrogen being replaced, apparently to the extent of 1, 2, or 3 eqs., by chlorine, bromine, nitrous acid, and amide; and in the last case they give rise to bases, of which aniline or phenylamine, $C_{12} H_7 N$, or $C_{12} \begin{matrix} H_2 \\ N H_2 \end{matrix}$, is the type. Here we see amide combined with the group $C_{12} H_2$, ($C_{12} H_2$ (benzole) minus H .) Hence aniline may be regarded as ammonia, $N H_3$, H , in which the last eq. of hydrogen is replaced by $C_{12} H_2$. To the group we give the name phenyle, and hence aniline is also called phenylamine. Benzole may be regarded as the hydride of phenyle. $C_{12} H_2, H$. Of course the homologues of benzole, namely toluole, xylene, and cumole, as they yield bases homologous with aniline, give rise to a series of groups of radicals, homologous with phenyle, and the general formula of which is $C_n H_n$ —, n . Since benzole, although derived from benzoic acid, which contains 14 eqs. of

	Benzene Series.	Toluene Series.	Xylylene Series.	Cumene Series.	Cymene Series.
Phenyle	$C_{12}H_6$	$C_{14}H_8$	$C_{16}H_{10}$	$C_{18}H_{12}$	$C_{20}H_{14}$
Hydrate of Phenyle; Benzole	$C_{12}H_6, H_2$	$C_{14}H_8, H_2$	$C_{16}H_{10}, H_2$	$C_{18}H_{12}, H_2$	$C_{20}H_{14}, H_2$
Chlorobenzole	$C_{12}H_5Cl$	$C_{14}H_7Cl$	$C_{16}H_9Cl$	$C_{18}H_{11}Cl$	$C_{20}H_{13}Cl$
Bromobenzole	$C_{12}H_5Br$	$C_{14}H_7Br$	$C_{16}H_9Br$	$C_{18}H_{11}Br$	$C_{20}H_{13}Br$
Nitrobenzole	$C_{12}H_5NO_2$	$C_{14}H_7NO_2$	$C_{16}H_9NO_2$	$C_{18}H_{11}NO_2$	$C_{20}H_{13}NO_2$
Dinitrobenzole	$C_{12}H_4N_2O_4$	$C_{14}H_6N_2O_4$	$C_{16}H_8N_2O_4$	$C_{18}H_{10}N_2O_4$	$C_{20}H_{12}N_2O_4$
Hydrated Oxide of Phenyle, Carboic Acid ..	$C_{12}H_6O, H_2O$	$C_{14}H_8O, H_2O$	$C_{16}H_{10}O, H_2O$	$C_{18}H_{12}O, H_2O$	$C_{20}H_{14}O, H_2O$
Phenylamine (Aniline)	$C_{12}H_7N$	$C_{14}H_9N$	$C_{16}H_{11}N$	$C_{18}H_{13}N$	$C_{20}H_{15}N$
Nitraniline	$C_{12}H_6N$	$C_{14}H_8N$	$C_{16}H_{10}N$	$C_{18}H_{12}N$	$C_{20}H_{14}N$
Dinitraniline	$C_{12}H_5N_2$	$C_{14}H_7N_2$	$C_{16}H_9N_2$	$C_{18}H_{11}N_2$	$C_{20}H_{13}N_2$
Chloraniline	$C_{12}H_5Cl$	$C_{14}H_7Cl$	$C_{16}H_9Cl$	$C_{18}H_{11}Cl$	$C_{20}H_{13}Cl$
Dichloraniline	$C_{12}H_4Cl_2$	$C_{14}H_6Cl_2$	$C_{16}H_8Cl_2$	$C_{18}H_{10}Cl_2$	$C_{20}H_{12}Cl_2$
Trichloraniline	$C_{12}H_3Cl_3$	$C_{14}H_5Cl_3$	$C_{16}H_7Cl_3$	$C_{18}H_9Cl_3$	$C_{20}H_{11}Cl_3$
Bromaniline	$C_{12}H_5Br$	$C_{14}H_7Br$	$C_{16}H_9Br$	$C_{18}H_{11}Br$	$C_{20}H_{13}Br$
Dibromaniline	$C_{12}H_4Br_2$	$C_{14}H_6Br_2$	$C_{16}H_8Br_2$	$C_{18}H_{10}Br_2$	$C_{20}H_{12}Br_2$

carbon, has itself only 12 eqs. of carbon, it cannot contain the radical benzole, but is itself a new radical, derived from it; just as acetylene, derived from ethylene, contains 2 eqs. of hydrogen less than ethylene. The preceding table will show some of the derivations of benzole, and indicate the homologous series to which each belongs. Only the compounds connected with benzole are there named, the formulæ only of those higher in the series being given.

A NEW CLASS OF ALCOHOLS.

We have already described acroleine, or the hydrated oxide of acryle, $C_3 H_4 O_2$, and acrylic acid, $C_3 H_4 O_3$. As these compounds have to each other the same relations as aldehyde has to acetic acid, it was natural to look for the alcohol of the series.

Will had shown that oil of mustard is the sulphocyanide of the radical allyle, $C_3 H_5$, which is isomeric, but not identical with propionyle.

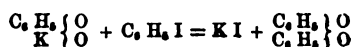
Berthelot and De Luca, by studying the action of iodide of phosphorus on glycerine (the substance which yields acroleine), obtained the compound $C_3 H_5 I$, which they called iodised propylene. And they further proved that when this iodide is acted on by sulphocyanide of potassium, there are formed iodide of potassium and oil of mustard, or sulphocyanide of allyle. Oil of mustard had already been artificially produced from oil of garlic, which is the sulphide of allyle, but the recent experiments confirm Will's view by forming oil of mustard by means of a different compound. It is now evident that the radical in the iodised propylene of Berthelot and De Luca is identical with the allyle of Will and Wertheim.

Hofmann and Cahours have now succeeded in obtaining not only the alcohol of this series, but many other compounds, and have shown that there exists a series of alcohols, of which we are about to describe one, running parallel to the two series of alcohols already known, the methylic and the benzoic series. They have named the radical of the new alcohol acryle, which is somewhat unfortunate, as that name was already given to the derived radical of acroleine and acrylic acid, corresponding to acetylene. It is not easy to see why they did not adopt the name allyle, already given to the same radical in oil of mustard and oil of garlic.

When iodide of allyle (for, to avoid confusing the reader, we shall retain the old name) is acted on by oxalate of silver, we obtain iodide of silver and oxalate of allyle, $C_3 H_5 O_2 = C_3 H_5, 2 (C_3 H O)$. This, acted on by ammonia, yields oxamide and allylic alcohol exactly as oxalate of ethylene yields oxamide and ethylic alcohol.

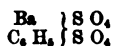
Allylic (or acrylic) alcohol, $C_3 H_5 O_2 = C_3 H_5, O, H O$, is isomeric with acetone and with propylaldehyde, but is quite distinct from these two substances. It burns with a luminous flame, and mixes with water in all proportions. It has a peculiar pungent odor, re-

sembling that of mustard, and this odor characterises, more or less, all the compounds of this series. When acted on by potassium, hydrogen is given off, and a transparent gelatinous mass is formed, corresponding to the substance formed when potassium acts on alcohol. The latter contains potassium, ethyle, and oxygen. The new body contains potassium, allyle, and oxygen. When this is acted on by iodide of allyle, iodide of potassium is formed, and oxide of allyle, or allylic ether, is separated, as a liquid lighter than water, and insoluble in it. The action is as follows:



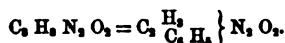
By distilling allylic alcohol with chloride, bromide, or iodide of phosphorus, the chloride, bromide, and iodide of allyle are easily obtained. With potash and bisulphide of carbon allylic alcohol yields a splendid yellow salt, corresponding to the xanthate of potassium.

With sulphuric acid, allylic alcohol forms an acid corresponding to sulphuric acid. The new acid forms a soluble salt with baryta:

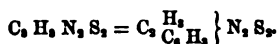


The carbonate, acetate, benzoate, oxalate, oxamate, and cyanate of oxide of allyle have all been formed and analysed.

The cyanate of allyle, with ammonia, yields fine crystals of allylurea:



If we suppose the 2 eq. of oxygen in this were to be replaced by sulphur, we have thiosinnamine, already described under oil of mustard, the formula of which is



Aniline forms with cyanate of allyle a corresponding compound, analogous to allylurea, which crystallises beautifully.

With water, cyanate of allyle yields diallylurea, $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2 = \text{C}_2\left\{\begin{smallmatrix}\text{H}_2 \\ \text{C}_6\text{H}_5\end{smallmatrix}\right\}\text{N}_2\text{O}_2$, which has been already mentioned as sinapoline, and represented as diallylic urea.

When cyanate of allyle is heated with potash, sinapoline rises to the surface, and an alkaline liquid distils over, which is a mixture of volatile bases. Among these have been already detected Methyllamine, Propylamine, and *Allylamine*, or *Acrylamine*, $\text{C}_3\text{H}_7\text{N} = \text{N}\left\{\begin{smallmatrix}\text{H}_2 \\ \text{C}_3\text{H}_5\end{smallmatrix}\right\}$. This new base boils between 180° and 190° ; but it has not yet been found possible to obtain its platinum salt crystallised.

These results prove incontestably the existence of a new series of alcohols, running parallel to that of the methylic and ethylic alcohols, and of a number of other series connected with this one, and parallel to the corresponding series connected with alcohol and acetic acid, so often referred to. The following table contains the formulæ of the compounds of the allylic or acrylic series hitherto obtained, along with those of the ethylic series.

Allylic or Acrylic Series		Ethylic Series.	
$C_3 H_5 O_2$	Alcohol.....	$C_2 H_5 O_2$	
$C_3 H_5 O$, or }.....	Oxide or Ether.....	$C_2 H_5 O$, or }	
$C_3 H_5 O_2$		$C_2 H_5 O_2$	
$C_3 H_5 Cl$	Chloride.....	$C_2 H_5 Cl$	
$C_3 H_5 Br$	Bromide.....	$C_2 H_5 Br$	
$C_3 H_5 I$	Iodide.....	$C_2 H_5 I$	
$C_3 H_5 S$, or }	Sulphide.....	$C_2 H_5 S$, or }	
$C_3 H_5 S_2$	Oil of Garlic. Sulphide of Ethyle	$C_2 H_5 S_2$	
$C_3 H_5, C_3 N S_2$ {	Sulphocyanide.	$C_2 H_5, C_2 N S_2$ {	
	Oil of Mustard. Sulphocyanide of Ethyle		
$C_3 (K, C_6 H_5) S_4 O_2$	Xanthate of potassium.....	$C_2 (K, C_6 H_5) S_4 O_2$	
$C_3 H_5 O, C_3 N O$	Cyanate.....	$C_2 H_5 O, C_2 N O$	
$C_3 (H_5, C_6 H_5) N_2 O_2$	Urea.	$C_2 (H_5, C_6 H_5) N_2 O_2$	
$C_3 (H_5, C_6 H_5) N_2 S_2$	Allylic and Ethylic {	$C_2 (H_5, C_6 H_5) N_2 O_2$	
	Sulphuretted Urea. Thiosinamine. ?		
$C_3 (H_5, 2 C_6 H_5) N_2 O_2$	Urea.	$C_2 (H_5, 2 C_6 H_5) N_2 O_2$	
	Diallyl. Diethyl. }		
$C_3 (C_6 H_5)_2 O_2$	Oxalate.....	$C_2 (C_6 H_5)_2 O_2$	
$C_3 H_5 (C_6 H_5) N O_2$	Oxamate.....	$C_2 H_5 (C_6 H_5) N O_2$	
$C_3 H_5 O, C_3 O_2$	Carbonate.....	$C_2 H_5 O, C_2 O_2$	
$C_3 H_5 O, C_3 H_5 O_2$	Acetate.....	$C_2 H_5 O, C_2 H_5 O_2$	
$C_3 H_5 O, C_3 H_5 O_2$	Benzoate.....	$C_2 H_5 O, C_2 H_5 O_2$	
$C_3 H_5 O, H O, 2 S O_2$	Sulpho-acid.....	$C_2 H_5 O, H O, 2 S O_2$	
$N H_2, C_3 H_5$	Amide base.....	$N H_2, C_2 H_5$	
$C_3 H_5 O_2$	Aldehyde.	$C_2 H_5 O_2$	
	Acrylic. Acetylo {		
$C_3 H_5 O_4$	Acid. Acetic {	$C_2 H_5 O_4$	
	Acrylic. Acetic {		
$C_3 H_5$	Hydrocarbon.	$C_2 H_5$	
	Propylene. Marsh gas }		

It will be seen that the analogy is perfect. The aldehyde of the new series is acroleine, or the hydrated oxide of the radical $C_3 H_5$, already known by the name of acryle, and corresponding to acetylo, $C_4 H_7$. Acrylic acid, also long known, is the hydrated teroxide of the radical $C_3 H_5$.

Now we have already seen that acrylic acid is one of the homologous series, of which we have named six members, namely, acrylic acid, the third; angelic acid, the fifth; moringic acid, the fifteenth; oleic acid, the eighteenth; dœglinic acid, the nineteenth; and erucic acid, the twenty-second in the series.

We cannot now doubt that, like acrylic acid, each of these, as well as each of the unknown members of the series, will be found to have a corresponding alcohol. These alcohols, whose existence implies, in each case, that of compounds corresponding to those in the table just given and many others, do not appear to occur in

nature; but it seems likely that they may be obtained from bodies like the iodide of allyle, $C_6 H_5 I$, as the allylic alcohol has been from that compound. Indeed, Hofmann and Cahours have already found that bromide of valeryle, $C_{10} H_9 Br$, undergoes changes similar to those seen in the iodide of allyle; and also that some of the compounds from olefant gas, probably iodide or bromide of acetyle, $C_4 H_5 I$, or $C_4 H_5 Br$, appear to yield analogous results.

We may here subjoin a short table, showing the relations of the new alcohols and their derived acids to the old alcohols and their derived acids:

Group of Alcohols.			Group of Acids.		
New.	Old.		New.	Old.	
$C_2 H_5 O_2$	$C_2 H_4 O_2$	Methylic	$C_2 O_4$	Carbonic †	$C_2 H_2 O_4$ Formic
$C_3 H_7 O_2$	$C_3 H_6 O_2$	Ethylic	$C_3 H_2 O_4$		$C_3 H_4 O_4$ Acetic
$C_4 H_9 O_2$	$C_4 H_8 O_2$	Propylic	$C_4 H_4 O_4$	Acrylic	$C_4 H_6 O_4$ Propylic
$C_5 H_{11} O_2$	$C_5 H_{10} O_2$	Butylic	$C_5 H_6 O_4$		$C_5 H_8 O_4$ Butyric
$C_6 H_{13} O_2$	$C_6 H_{12} O_2$	Amylic	$C_6 H_8 O_4$	Angelic	$C_6 H_{10} O_4$ Valeric
$C_7 H_{15} O_2$	$C_7 H_{14} O_2$	Hexylic	$C_7 H_{10} O_4$		$C_7 H_{12} O_4$ Caproic
$C_8 H_{17} O_2$	$C_8 H_{16} O_2$	Heptylic	$C_8 H_{12} O_4$		$C_8 H_{14} O_4$ Ceanthyl
$C_{10} H_{21} O_2$	$C_{10} H_{20} O_2$	Octylic	$C_{10} H_{14} O_4$		$C_{10} H_{16} O_4$ Caprylic
*	*	*	*	*	*
*	*	*	*	*	*
$C_{28} H_{58} O_2$	$C_{28} H_{56} O_2$		$C_{28} H_{54} O_4$ Oleic		$C_{28} H_{56} O_4$ Stearic

There are many blanks in this small extract, as it were, from the entire table. But these will rapidly be filled up.

A NEW CLASS OF ACIDS.

There is a series of bibasic acids, running parallel to the monobasic volatile acids of the formylic series. In the benzoic group there is also a series of monobasic volatile acids, of which benzoic acid is the type, and which, like the acids of the formylic series, contain, in the hydrated state, 4 eqs. of oxygen.

Now, Hofmann has found that cuminic acid, one of the acids of the benzoic series, the formula of which is $C_{20} H_{12} O_4$, when boiled with chromic acid, is converted into a new acid, which he calls

Insolinic Acid, $C_{18} H_8 O_6 = C_{18} H_8 O_5, 2 H O$. This acid is insoluble in alcohol and ether, and it bears to one of the acids of the benzoic series a relation similar to that which exists between oxalic acid and formic acid. For insolinic acid is bibasic, like oxalic acid, and it will be seen, by the following table, that it contains 2 eqs. of carbonic acid more than the corresponding monobasic acid, just as oxalic acid is formic acid *plus* 2 eqs. of carbonic acid. The series of the monobasic aromatic acids is itself very imperfect, and of the corresponding bibasic acids two only are known, namely, insolinic acid, and phthalic acid, the latter having been recognised as a member of this series, in consequence of the discovery of insolinic acid.

Monobasic Aromatic Acids.

$C_{14}H_8O_4$ Benzoic
 $C_{15}H_8O_4$ Toluyllic
 $C_{18}H_{10}O_4$?
 $C_{20}H_{12}O_4$ Cuminic

Bibasic Acids.

$C_{16}H_8O_6$ Phtalic
 $C_{18}H_8O_6$ Insolinic
 $C_{20}H_{10}O_6$?
 $C_{22}H_{12}O_6$?

Thus we see, that in another quarter a new homologous series of acids has been detected. We have now the formyllic series of acids, the oxalic series of bibasic acids, the acrylic series monobasic, the benzoic series monobasic, and the phtalic series bibasic. It will be observed, that while the two monobasic series, the formyllic and benzoic, have each a parallel bibasic series, the monobasic acrylic series has, as yet, no such bibasic series parallel to it. But if to acrylic acid, $C_3H_4O_2$, we add $2CO_2$, which is the difference between formic and oxalic acids, we obtain the formula $C_5H_4O_6$, which is that of maleic and fumaric acids, well-known bibasic acids, $C_5H_4O_6, 2H_2O$. The next acid in this series will be $C_{10}H_4O_6 = C_{10}H_4O_6, 2H_2O$; and this is the formula of itaconic and citraconic acids, both bibasic. I think it very probable, therefore, that some of the acids just named will prove to belong to a bibasic series, parallel to the acrylic series, and differing from it by 2 eqs. of carbonic acid. And thus we see how every discovery in organic chemistry tends to reduce all known compounds to homologous series. The homology of maleic and fumaric acids, with itaconic and citraconic acids, has not, till now, attracted notice, but the discovery of insolinic acid has not only found a place for phtalic acid, but enabled us to perceive that the vegetable acids just named may also have their place in a series not remotely connected with that of alcohol, or rather with that of acrylic alcohol, and with that of the glycerides.

NEW PHOSPHORISED BASES.

Thénard, as already mentioned, has shown that methyle can replace the hydrogen in phosphuretted hydrogen, PH_3 , and thus give rise to new bases.

Hofmann and Cahours have recently, by adopting a new method, greatly extended our knowledge of these. The process consists in the action of terchloride of phosphorus on zincomethyle, zincethyle, zincamyle, &c., when chloride of zinc is formed, along with the base.

The bases thus obtained are volatile, and correspond to ammonia, in which the nitrogen is replaced by phosphorus, the hydrogen by methyle, &c. The compounds PMe_3 , analogous to cacodyle, $AsMe_3$, and PMe_3 , analogous to ammonia, were obtained by Thénard.

Hofmann and Cahours have not only obtained the compounds PAc , and $PAyl$, but by the action of the iodides of methyle, ethyle, and amyle on these, have formed a number of ammonium bases, analogous to tetramethylum. These last are obtained as iodides, from which, by the action of oxide of silver, the hydra-

ted oxides are obtained, which in properties are analogous to Hofmann's hydrated oxides of tetramethylum and tetrethylum, &c. The following table contains the formulæ of the radicals, bases, or iodides of radicals which they have obtained.

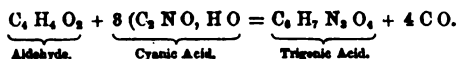
P Me ₃ *	* Me = C ₂ H ₅	P Ae ₃ } I	
P Me ₂		P Ayl } I	
P Me ₂ I		P Ayl ₂ †	† Ayl = C ₂₀ H ₄₁
P Me ₂ } I		P Ayl ₂ I	
P Aet	† Ae = C ₄ H ₉	P Ayl ₂ } I	
P Ae ₂ I		Me	
P Ae ₂ } I		P Ayl ₂ } I	
Me		Ae	

The iodides in this table, acted on by the oxide of silver, yield the hydrated oxides of the several ammonium radicals, and from these the other salts are obtained. At present we have only the general results. The details will soon be published.

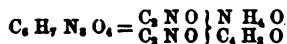
It appears, as might be anticipated from the existence of cacodyle and arsenethyle, that arsenic yields a series of similar compounds, and doubtless the other metals which have been shown to combine with radicals of the ethylic series will be found to yield compounds, analogous to some, if not all the above.

TRIGENIC ACID.

This acid is formed, along with other substances, when the vapor of hydrated cyanic acid is brought in contact with aldehyde. It is first obtained mixed with cyamelide and aldehydammonia, but the whole mass is dissolved in hydrochloric acid of moderate strength, and boiled as long as aldehyde is given off. On cooling, trigenic acid is deposited in small prisms, sparingly soluble in water, nearly insoluble in alcohol. Its formula is $C_4H_4N_2O_4 = C_4H_4N_2O_4, HO$, and it is monobasic. The silver salt is somewhat soluble in hot water, and is deposited on cooling in very minute crystalline spherical concretions, which become violet in the light. Leaving out of view the other products, which are secondary, the formation of the acid is explained as follows :



This acid contains the elements of anhydrous cyanic acid and of aldehydammonia.



SUDORIC ACID.

According to Favre, this acid exists in combination with potash and soda in the sweat. It is not yet known in a state of perfect purity, but its concentrated solution does not crystallise, and, when heated, gives off ammonia. Favre analysed a mixture of sudorate

of silver with chloride of silver, and obtained results from which, after deducting the chloride, he calculated for the sudorate of silver the formula $C_{10} \begin{matrix} H_8 \\ Ag \end{matrix} \left\{ \begin{matrix} N O_{14} \\ \end{matrix} \right.$; so that the acid will be $C_{10} H_8 N O_{14} = C_{10} H_8 N O_{11}, HO$. If this be confirmed, it is interesting as indicating some relation between sudoric acid and uric acid, as well as xanthic oxide and inosinic acid, all of which contain 10 eq. of carbon.

The salts of this acid with bases are all very soluble, but do not crystallise. This circumstance makes their purity somewhat doubtful. These salts are also soluble in absolute alcohol, except the silver salt.

THYMINÉ.

This name has been given by Gorup Besanex to a new base, found by him in the thymus gland of the calf. This is extracted by cold water, after removing as much fat as possible, and yields a reddish, very acid, liquid, which when evaporated deposits a brown coagulum. The supernatant liquid is quite limpid; baryta precipitates from it the phosphoric acid. The filtered liquid, when evaporated, forms caseous pellicles, consisting of carbonate of baryta and organic matter, and leaves a brown syrupy liquid, with an odor of soup. The addition of alcohol or ether causes slowly a deposit of impure thymine; which is purified by solution in boiling alcohol, and is deposited on cooling, as a shining powder, formed of minute crystals. 25 lbs. of the thymus gland yielded by this process only 3 or 4 grains of thymine.

It has neither taste nor smell; is very soluble in water, soluble in hot alcohol, insoluble in cold alcohol, in absolute alcohol, or in ether. Heated in a tube it melts, yielding a crystalline sublimate and alkaline vapors with a smell like that of hydrocyanic acid. Its salts are crystallisable. The hydrochlorate and sulphate are both efflorescent; the chloroplatinate forms octohedra, soluble in water, insoluble in alcohol.

THE THEORIES OF CHEMISTRY.

The late discoveries in organic chemistry have done as much, perhaps, to confuse our notions upon the theory of the arrangement of atoms, as they have to elucidate them. But although there appears a great discrepancy among chemical philosophers in regard to the true theory of the arrangement of the atoms in an organic compound, still the late discoveries of a great mass of facts are but paving the way for that great attainment. The remarks of Professor Gregory upon this subject are not irrelevant here, and are not only significant upon the subject of chemical theory, but present the wonderful fertility of organic combinations in a striking light.

Let us briefly recapitulate the different classes of compounds

treated of in this section, and represented in the table. This will best be done in a tabular form, and the reader will bear in mind that the vertical list here given corresponds to the horizontal line of the table of homologous compounds, which is only a selection from it, and that each number here given is the starting-point of a series of homologous compounds, the formulæ of which are obtained by simply adding C, H, successively to the formulæ of the methyle compounds, here taken as the lowest in the series.

Now, when it is considered that all of the compounds in the following table, known as the methyle and formyle series, and all that of ethyle and acetylene; that each of these 37 compounds is the starting-point of an homologous series, like that of fatty and oily acids, No. 29, which have been described; and that several of the numbers, namely, Nos. 12, 14, 15, 16, 17, 18, 19, 20, 21, 25 and 35, being bases, combine with all acids, and that each salt thus formed is also the starting-point of a similar series; that the bodies under Nos. 13 (of which there are several, such as oxalovinic, tartrovinic, phosphovinic, and carbovinic acids, not mentioned in the table) and 29, being acid, combine with all bases, and that each salt thus formed is the starting-point of a new homologous series; that the radicals and bases, from No. 14 to No. 22, all admit of substitution of one radical for another, yielding new bases, and consequently new salts *ad infinitum*; and finally, that probably every compound in the table admits of the substitution of chlorine, bromine, iodine, and nitrous acid for part of its hydrogen, thus yielding other inexhaustible series of new compounds, it will be seen, that even this formidable list, and the large table, are nothing more than short extracts from the real list of possible and probable compounds, producible by art, besides the infinite variety of nature. And yet, bearing in mind the laws of homologous compounds, and of substitutions, the whole of this immense mass of formulæ becomes easily intelligible, inasmuch that with a knowledge of one such series as has just been partially exemplified, any one may construct for himself a table including all, which, however, if printed at full length, even in the abbreviated shape of formulæ, would fill a volume. And all this refers only to the compounds connected with, or derived from, one series of radicals, that of methyle and ethyle. Nature, however, uses not only these, but many others, as yet less known to us, to produce her organised products. We trust that the study of this section will enable the student to grasp the principle, and to see his way through the seeming chaos of organic chemistry.

Of those radicals which do not belong to the series of ethyle and methyle (the best known), those most interesting are phenyle, C₆H₅, and its homologues, with some of their derivatives. As these may all be derived from the oil of tar, we have described them and their derivatives under that head. We shall then see that these radicals agree with those of the methyle series in re-

TABLE OF RADICALS AND THEIR DERIVATIVES FORMING THE FOUNDATIONS OF HOMOLOGOUS SERIES.

Compounds.	General Formula.	Example.
1. Electro-positive Radicals.....	$\text{Ca H}_2 + 1, \text{O}$	Ca H_2 , Methyle.
2. Oxides of ditto, or Ethers.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Oxide of Methyle.
3. Hydrated Oxides of ditto, or Alcohols.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Hydrate of Methyle.
4. Hydrates of ditto. Series of Marsh Gas.....	$\text{Ca H}_2 + 1, \text{Cl}$	$\text{Ca H}_2 \text{Cl}$, Chloride of Methyle.
5. Chlorides of ditto.....	$\text{Ca H}_2 + 1, \text{Cl}$	$\text{Ca H}_2 \text{Cl}$, Chloride of Methyle.
6. Bromides of ditto.....	$\text{Ca H}_2 + 1, \text{Br}$	$\text{Ca H}_2 \text{Br}$, Bromide of ditto.
7. Iodides of ditto.....	$\text{Ca H}_2 + 1, \text{I}$	$\text{Ca H}_2 \text{I}$, Iodide of ditto.
8. Sulphurets of ditto.....	$\text{Ca H}_2 + 1, \text{S}$	$\text{Ca H}_2 \text{S}$, Sulphuret of ditto.
9. Sulphurets + H S, or Mercaptans.....	$\text{Ca H}_2 + 1, \text{S}, \text{H S}$	$\text{Ca H}_2 \text{S}$, H S, Methyle Mercaptan.
10. Cyanides of Radical.....	$\text{Ca H}_2 + 1, \text{C}, \text{N}$	$\text{Ca H}_2 \text{CN}$, Cyanide of Methyle.
11. Sulphocyanides of ditto.....	$\text{Ca H}_2 + 1, \text{C}, \text{N}, \text{S}$	$\text{Ca H}_2 \text{CS}$, Sulphocyanide of ditto.
12. Salts of Oxides of ditto.....	$\text{Ca H}_2 + 1, \text{O}, \text{X}^*$	$\text{Ca H}_2 \text{O}$, X*, Salts of Oxide of ditto.
13. Acid Salts of ditto.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}, 2\text{Z}^\dagger$	$\text{Ca H}_2 \text{O}$, H O 2Z, Acid Salts.
14. Zincoradicals.....	$\text{Ca H}_2 + 1, \text{Zn}$	$\text{Ca H}_2 \text{Zn}$, Zincomethyle.
15. Stibioradicals.....	$\text{Ca H}_2 + 1, \text{Sb}$	$\text{Ca H}_2 \text{Sb}$, Stibiomethyle.
16. Arbio-Metallie ditto.....	$\text{Ca H}_2 + 1, \text{As}$	$\text{Ca H}_2 \text{As}$, Arbiomethyle.
17. Phosphoradicals.....	$\text{Ca H}_2 + 1, \text{P}$	$\text{Ca H}_2 \text{P}$, Phosphomethyle.
18. Amidic Bases.....	$\text{Ca H}_2 + 1, \text{N}$	$\text{Ca H}_2 \text{N}$, New Base.
19. Amide Bases.....	$\text{Ca H}_2 + 1, \text{N}, \text{H}$	$\text{Ca H}_2 \text{NH}$, Methylamine.
20. Nitrylic Bases.....	$\text{Ca H}_2 + 1, \text{N}, \text{H}$	$\text{Ca H}_2 \text{NH}$, Dimethylamine.
21. Ammonium Bases or Metals.....	$\text{Ca H}_2 + 1, \text{N}, \text{H}$	$\text{Ca H}_2 \text{NH}$, Trimethylamine.
22. Oxides of ditto.....	$\text{Ca H}_2 + 1, \text{O}$	$\text{Ca H}_2 \text{O}$, Tetramethylum.
23. Hydrated Oxides of ditto.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Oxide of ditto.
24. Salts of ditto.....	$\text{Ca H}_2 + 1, \text{O}, \text{X}^*$	$\text{Ca H}_2 \text{O}$, X*, Salts of ditto.
25. Electro-negative Radicals.....	$\text{Ca H}_2 + 1, \text{O}$	$\text{Ca H}_2 \text{O}$, Acetylo-urea.
26. Hydrated Oxides of ditto, or Aldehydes.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Formic Aldehyde.
27. Acids of ditto, or Volatile Oily Acids.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Formic Acid.
28. Amides of Acids.....	$\text{Ca H}_2 + 1, \text{O}, \text{N}$	$\text{Ca H}_2 \text{ON}$, Formamide.
29. Nitryles of Acids.....	$\text{Ca H}_2 + 1, \text{O}, \text{N}$	$\text{Ca H}_2 \text{ON}$, Formonitryle.
30. Hydrates of Electro-positive Radicals. Olefant Gas Series.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}, \text{C}$	$\text{Ca H}_2 \text{O}$, Hydrate of Methyle.
31. Nitriles of Acids.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}, \text{C}$	$\text{Ca H}_2 \text{O}$, Acetonitrile.
32. Sulphocyanides of Oxide of Radical No. 2.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}, \text{C}, \text{S}$	$\text{Ca H}_2 \text{OS}$, Sulphocyanide of Oxide of Methyle.
33. Pratinised Bases.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}, \text{P}$	$\text{Ca H}_2 \text{OP}$, New Base (besides others).
34. Bile Acid Series.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Oxalic Acid.
35. Oleic Acid Series.....	$\text{Ca H}_2 + 1, \text{O}, \text{H O}$	$\text{Ca H}_2 \text{O}$, Oleic Acid.

* X stands here for any hydrated acid, such as sulphuric, nitric, oxalic, acetic, benzoic, &c. These are so numerous, that only a general formula is given.

† Z stands here for any anhydrous acid. This formula includes sulphuric, carbonic, and other acids, and their homologues.

‡ As the reader knows, there are at least three series of homologues of methyle above; one only is given here.

§ The first acid in this series, oxalic acid, contains no hydrogen in the anhydrous acid. But all those higher in the scale contain hydrogen; as sebacic acid, $\text{Ca H}_{18} \text{O}_8$, 2 H O.

placing hydrogen in ammonia, and in giving rise to a large number of bases and other interesting products.

Before quitting the subject of the radicals of the methyle and ethyle series, $C_n H_n + 1$, and their derivatives, it must be mentioned that different views have been taken of these compounds besides that here adopted. Some consider alcohol and ether to be compounds of $C_2 H_6$ or ethylene, with water; but this view is now generally abandoned. But the views taken by Kolbe, and those of Williamson, must be noticed. Kolbe admits the existence of the methyle series of radicals, but not that of the derived acid radicals of the formyle series, $C_n H_n - 1$. According to him, the acids of the formic series are coupled oxalic acids, the copula being in each case a radical of the methyle series. The following table exhibits together the view already adopted in this work, and that of Kolbe, for the first six acids of the series, $(C_n H_n)_2 O_4$:

	Kolbe.			Kolbe.	
Formic acid	C_2	H_2	O_2	$H O =$	$C_2 O_2, H O = C_2, H_2, O_4$
Acetic acid	C_4	H_6	O_4	$H O =$	$C_4 H_6, C_2 O_2, H O = C_4, H_4, O_4$
Propylic acid	C_6	H_8	O_4	$H O =$	$C_6 H_8, C_2 O_2, H O = C_6, H_6, O_4$
Butyric acid	C_8	H_{10}	O_4	$H O =$	$C_8 H_{10}, C_2 O_2, H O = C_8, H_8, O_4$
Valerianic acid	C_{10}	H_{12}	O_4	$H O =$	$C_{10} H_{12}, C_2 O_2, H O = C_{10}, H_{10}, O_4$
Caproic acid	C_{12}	H_{14}	O_4	$H O =$	$C_{12} H_{14}, C_2 O_2, H O = C_{12}, H_{12}, O_4$

It will be seen that in the first column the acid radicals formyle, acetylene, propionyle, butyryle, valeryle, and caproyle, are supposed to be united to 3 eqs. of oxygen and 1 of water; while in the second, hydrated oxalic acid, $C_2 O_2, H O$, is supposed to be coupled, first with hydrogen, and then with the homologues of hydrogen, the basic radicals methyle, ethyle, propyle, butyle, and amyle. It is evident that either view sufficiently accounts for the great analogy of these acids among each other, and that the latter perhaps accounts better for the fact that the ammonia salts of these radicals yield the cyanides of the basic radicals they are supposed to contain. Thus acetate of ammonia yields cyanide of methyle, propylate of ammonia, cyanide of ethyle, &c. On the whole, it is impossible as yet to give to the one view a decided preference over the other; and it will be seen that Kolbe's view may easily be applied to all compounds supposed, on the other theory, to contain formyle, acetylene, and the radicals of that series. Kolbe has, indeed, with much ingenuity, extended it to all these and many analogous products, such as aldehyde, including those of substitution, chloral, chloroacetic acid, and the chlorinised ethers generally. But our limited space forbids us to enter into these details, and we therefore stop, recommending to the student to bear in mind, that not only the doctrine of compound radicals, but also that of coupled compounds, probably, has a great share in the production of organic bodies.

Williamson follows Berzelius in not regarding alcohol as the hydrated oxide of ethyle, $C_2 H_5 O, H O = C_2 H_5 O_2$, but as having only half this atomic weight, $C_2 H_5 O$; and in consequence of some

very remarkable discoveries of his own, he finds it necessary to halve the equivalent of hydrogen, and to write the formula of water $\text{H}_2 \text{O}$, and that of alcohol, $\text{C}_2 \text{H}_5 \text{O}$. He supposes alcohol to be water, in which one-half of the hydrogen is replaced by the body $\text{C}_2 \text{H}_5$ (which, with the double or usual equivalent of hydrogen, would be $\text{C}_2 \text{H}_4$, hence the reason for halving the eq. of hydrogen), thus: water $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}$; alcohol

$\left. \begin{smallmatrix} \text{H} \\ \text{C}_2 \text{H}_5 \end{smallmatrix} \right\} \text{O}$. According to this view, ether is water in which both the eqs. of hydrogen (that is, all the hydrogen) have been replaced by $\text{C}_2 \text{H}_5$; water $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}$; ether $\left. \begin{smallmatrix} \text{C}_2 \text{H}_5 \\ \text{C}_2 \text{H}_5 \end{smallmatrix} \right\} \text{O} = \text{C}_4 \text{H}_{10} \text{O}$ (=, in the ordinary form, $\text{C}_4 \text{H}_8 \text{O}$).

We have already explained that if, without altering the atomic weight of hydrogen, we represent water thus: $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}$; alcohol

will be $\left. \begin{smallmatrix} \text{H} \\ \text{C}_2 \text{H}_5 \end{smallmatrix} \right\} \text{O}$, and ether $\left. \begin{smallmatrix} \text{C}_2 \text{H}_5 \\ \text{C}_2 \text{H}_5 \end{smallmatrix} \right\} \text{O}$. This amounts, as will be perceived, to the same thing as Williamson's view, and it must be borne in mind, that many other facts render it probable that the true formula for water is a double one, or that the molecule of water, which is the most frequent type of organic compounds, contains 2 at. of hydrogen and 2 of oxygen.

The strongest arguments for this view are derived from the fact, observed by Williamson, that alcohol is converted into ether by the action of iodide of ethyle on a solution of potash in alcohol. According to the usual view, this change would be thus represented: $\text{C}_2 \text{H}_5 \text{O} + \text{K O} + \text{C}_2 \text{H}_5 \text{I} = \text{K I} + 2 (\text{C}_2 \text{H}_5 \text{O})$, the potash being supposed to have replaced the water of alcohol. Williamson supposes one-sixth of the hydrogen in alcohol to have been replaced by potassium,

thus: $\text{C}_2 \text{H}_5 \text{O} + \text{K O} = \text{H O} + \text{C}_2 \left. \begin{smallmatrix} \text{H}_5 \\ \text{K} \end{smallmatrix} \right\} \text{O}$ (halving the eq. of

potassium). Then this compound, acted on by iodide of ethyle, which he makes $\text{C}_2 \text{H}_5 \text{I}$ (halving the eq. of iodine also), yields ether with it, thus: $\text{C}_2 \left. \begin{smallmatrix} \text{H}_5 \\ \text{K} \end{smallmatrix} \right\} \text{O} + \text{C}_2 \text{H}_5 \text{I} = \text{K I} + \left. \begin{smallmatrix} \text{C}_2 \text{H}_5 \\ \text{C}_2 \text{H}_5 \end{smallmatrix} \right\} \text{O}$. To

decide between the two theories, Williamson tried to replace one of the eqs. of hydrogen by methyle. If the ordinary view were right, he should have obtained a mixture of oxide of ethyle and oxide of methyle, by causing iodide of methyle to act on the potash compound of ether, $\text{C}_2 \text{H}_5 \text{O} + \text{K O} + \text{C}_2 \text{H}_5 \text{I} = \text{K I} + \text{C}_2 \text{H}_5 \text{O} + \text{C}_2 \text{H}_5 \text{O}$ (using the ordinary equivalents); but instead of this, he obtained a new alcohol, $\text{C}_3 \text{H}_7 \text{O}$. This he explains as follows. In

his notation, iodide of methyle is $\text{C H}_3 \text{I}$. Hence $\text{C}_2 \left. \begin{smallmatrix} \text{H}_5 \\ \text{K} \end{smallmatrix} \right\} \text{O} + \text{C H}_3 \text{I} = \text{K I} + \left. \begin{smallmatrix} \text{C}_2 \text{H}_5 \\ \text{C H}_3 \end{smallmatrix} \right\} \text{O}$. This latter body, $\text{C}_3 \text{H}_7 \text{O}$, in ordi-

nary notation, C_6H_4O or $C_6H_5O_2$, is a very remarkable new alcohol, and Williamson has obtained others of the same class, which, however, as well as the first, have not yet been fully described. These remarkable researches will probably hereafter lead to modifications of our views on many points; but, in the mean time, we shall adhere to the usual view, which, for the moment, is the best attainable, but which, like all theories, must in time give place to such as better agree with all known facts. A theory in chemistry is nothing more than such a view as groups together the largest number of facts at a given time, and has no pretensions to absolute truth, nor to be more than a guide to the inquirer, and an aid to his memory.

ACTION OF HYPONITROUS ACID ON ARTIFICIAL BASES.

It is necessary here to notice the remarkable change produced on compounds of the class of organic bases, and on others derived from ammonia, such as amides, &c., by hyponitrous acid. The reaction is attended by the formation of water, of free nitrogen, and of an oxidised product. We have mentioned some examples of it incidentally, as that of the conversion of alanine into lactic acid; but this peculiar method of oxidation seems destined very much to extend our power of artificially producing or reproducing organic bodies. Piria has shown that oxamide, succinamide, butyramide, and asparamide or malamide, are thus converted into oxalic, succinic, butyric, and malic acids. Let NH_2X be = any amide. Then $NH_2X + NO_2 = 2HO + N_2 + XO$. And in the case of oxamide we have $NH_2C_2O_2 + NO_2 = 2HO + N_2 + C_2O_2$. Strecker has found that hippuric acid, glycocine, alanine, and leucine, are thus converted into the acids $C_{10}H_8O_6$, $C_4H_4O_6$, $C_6H_6O_6$, and $C_{12}H_{10}O_6$. Now, it is important to know what is the result of the action of hyponitrous acid on the bases. Hunt found that aniline, when its hydrochlorate is warmed with hyponitrite of silver, yields chloride of silver, nitrogen, and hydrated oxide of phenyle exactly as might be expected. $C_6H_5N, HCl + AgO, NO_2 = AgCl + N_2 + C_6H_5O, HO + 2HO$. Now this compound bears to aniline the same relation as alcohol does to ethylamine, and it was therefore to be expected that ethylamine with NO_2 would yield alcohol $C_2H_5 + NNO_2 = HO + N_2 + C_2H_5O, HO$. But Hofmann has found the reaction to be somewhat different; 2 eqs. of NO_2 act on 1 eq. of ethylamine, and give rise to hyponitrite of oxide of ethyle, $C_2H_5N + 2NO_2 = (C_2H_5O, NNO_2) + N_2 + 2HO$. Here, then, we have formed from the base, not the hydrated oxide, but the anhydrous oxide of the radical ethyle, which has combined with the second eq. of NO_2 . But from the hyponitrite the alcohol or hydrated oxide may be obtained, by the action of sulphohydrate of potassium, $(C_2H_5O, NNO_2) + 6(KS, HS) = (C_2H_5O, HO) + NH_3 + 2HO + 6KS$. Hence it will be possible, if we can

obtain any base, the alcohol of which is unknown, to obtain the alcohol as above. - Hofmann has done so with amylamine and propylamine, as well as ethylamine, or has shown that it may be done, although he has not yet described the propylic alcohol. But there can now be no doubt, that if we could obtain propylamine, butylamine, caprotylamine, or any of the bases of that series, in considerable quantity, as we may one day be able to do, from the oil of tar or animal oil, we shall then be able to obtain the hyponitrites, and from these the hydrates of the oxides, $C_3 H_7 O$, $C_4 H_9 O$, $C_6 H_{13} O$, &c.; that is, the propylic, butylic, and caprotylic alcohols. In general, the action of hyponitrous acid on all the known artificial bases should be carefully studied.

Propyle. $C_3 H_7$. Pro. This radical is homologous with the radical methyle. It is found when butyric acid is decomposed by the voltaic battery.

There is an *oxide of propyle*, or *Propylic Ether*, $C_3 H_7 O$.

The *Hydrated Oxide of Propyle* is an alcohol. $C_3 H_7 O, H O = Pr O, H O$. It resembles common alcohol in its chemical relations. The radical propyle combines with the homologous chlorine, iodine, bromine, cyanogen, and sulphur. These compounds are analogous to those of ethyle.

Propylamine is a volatile base homologous with ammonia and methylamine.

Propionyle is a radical homologous with acetylc, but has not yet been isolated. Its compounds are homologous with those of acetylc.

Propional is the alcohol of propionyle, $C_3 H_7 O, H O = C_3 H_7 O, H O = Pr O, H O$. It is a volatile oily liquid, having the characters of an aldehyde, and yielding propylic acid by oxidation.

Hydrated Propylic Acid, $C_3 H_7 O_2, H O = C_3 H_7 O_2, H O = Pr O_2, H O$, possesses oily properties, and is the next above acetic acid in the series of volatile acids.

Propione, $C_3 H_7 O$ or $C_{10} H_{13} O_2$, is homologous with actone. It is a fragrant oily volatile liquid.

Propylamide, $C_3 H_7 O_2, N H_2$, is analogous to acetamide. It is formed when ammonia acts on propylate of oxide of ethyle. When heated with anhydrous phosphoric acid, it yields propionitryle, which is cyanide of ethyle.

Gerhardt has proposed to name the electro-positive radicals of the methylic series, standing above ethyle in the list, in a way which indicates their place in the series. Thus, he names propyle, *trityle*, as being the third member of the series; butyle, the fourth, will be *tetrtyle*; amyle, the fifth, will be *pentyle*, and so on. It is not unlikely that this nomenclature may be adopted for these radicals, while those of the formylic series shall retain names derived from the acids in which they are supposed to exist.

It will be observed, that all the compounds of propyle, $C_3 H_7$, and of its derived radical, propionyle, $C_3 H_7$, which, so far as known,

have been briefly described in the preceding pages, correspond perfectly to those of methyle and ethyle, and of their derivatives, formyle and acetylene. And it cannot be doubted, that we shall in time discover for every compound of methyle or of formyle, a corresponding one of propyle and propionyle, as we have of ethyle and acetylene. The properties of these compounds may even now be confidently predicted to a great extent. Thus we shall have a zincopropyle, a stibiopropyle, &c., with properties closely resembling those of the ethyle compounds.

Before quitting this subject, it may here be mentioned, that oil of garlic, $C_6 H_4 S$, and oil of mustard, $C_6 H_4 C_2 N S_2$, contain a radical *allyle*, $C_3 H_5$, isomeric with propionyle, but not identical with it. At least the oxide of allyle, which is known, does not possess the properties which we should expect to find in oxide of propionyle. It is probable that allyle and propionyle may prove to be isomeric only.

Butyle. $C_4 H_9$ Bu.—This radical, discovered by Kolbe, is obtained among the products of the decomposition, by the galvanic current, of valerianic or valeric acid, $C_{10} H_{19} O_4$, thus: $C_{10} H_{19} O_4 = C_4 H_9 + 2 C_3 O + H$. It is a colorless transparent liquid, of an agreeable ethereal smell, and a taste at first slight, afterwards burning. It is insoluble in water, soluble in alcohol and ether. It boils at $226^\circ F$, is inflammable, and burns with a luminous but smoky flame. Its density in the liquid state, at 64° , is 0.694; that of its vapor is 4.053.

There is a chloride and cyanide of butyle, Bu Cl and Bu Cy.

Butylamine, $C_4 H_{11} N$, is an oxide base, and is isomeric with the amide bases diethylamine and methylopropylamine.

The radical *Butyryle*, $C_4 H_7$, has not been isolated. There is a hydride of this radical, $C_4 H_7, H$, which is likewise termed butylene and tetrylene. It is homologous with olefiant gas.

The *Butyrate of Oxide of Ethyle*, $C_4 H_7 O, C_2 H_5 O_2$, is one of the fragrant ethers resembling the pineapple, melon, and strawberry. It is butyric acid, combined with the oxide of ethyle.

The radicals containing C_{10} form a number of interesting compounds. With *Amyle*, the oxide of that radical, the *hydrated oxide*, the *sulphanylic acid*, the *carbonide of oxide of amylen*; and also, with nitrogen, strong bases, which will be found under the head of organic bases.

The radicals containing C_{11} form likewise an interesting series of compounds, many of which will be found in their places in this volume.

The radical *Caprotyle*, $C_{11} H_{23}$, gives rise to the oxide and hydrated oxide of that radical. There is obtained all the compounds of this radical belonging to the other radicals, as the cyanide, &c. It is homologous with formyle.

There is a radical with C_{17} , termed *Heptyle* or *Enanthyle*, al-

though not yet isolated. The radicals with C_{16} are *Octyle*, $C_{16}H_{17}$, and *Capryle*, $C_{16}H_{15}$, and correspond to methyle and formyle.

The radicals with C_{18} are termed *Nonyle*, $C_{18}H_{19}$, and *Pelorgyle*, $C_{18}H_{17}$.

The radicals containing C_{20} is termed *Capryle* or *Rutyle*, $C_{20}H_{19}$.

The radicals containing C_{22} are *Cetyle*, $C_{22}H_{23}$, and *Palmityle*, $C_{22}H_{21}$.

The radicals with C_{24} are only known as containing $C_{24}H_{25}$. Those of $C_{24}H_{23}$ are yet unknown.

The radicals with C_{26} are known, as $C_{26}H_{27}$, but those containing $C_{26}H_{25}$ are not yet known.

These radicals all form interesting compounds, some of which are of late discovery, and are of great importance, both in a scientific and practical view. As the carbon of these compounds increases they assume the appearance of oils, until finally, with the still greater increase of carbon, they become hard, or fatty and waxy.

Preparation of Methylc Alcohol.—Kane's process for the preparation of methylc alcohol, by saturating crude wood-spirit with chloride of calcium and distilling with water, yields but a small quantity of the pure product, in most cases not more than 2 or 3 oz. from a gallon of the crude wood-spirit. A much better result is obtained by first treating the crude spirit with a caustic alkali. When crude wood-spirit is mixed with an equal volume of a strong solution of caustic potash or soda, a tolerably strong action takes place, accompanied by a rise of temperature and formation of a homogeneous solution, which, when distilled, yields a distillate containing a considerable quantity of methylc alcohol, and a residue consisting of acetate of potash or soda, with a small quantity of resinous matter. On desiccating the distillate with carbonate of potash, saturating with dry chloride of calcium, and distilling at 100° to remove oils and acetone, then decomposing the compound of methylc alcohol and chloride of calcium by water in the usual manner, and dehydrating the distillate with quick-lime, a quantity of pure methylc alcohol is obtained, very much larger than that which can be procured without the use of caustic alkali.

The liquid distilled from the methylated chloride of calcium was treated with a solution of caustic potash, which separated some oils, mixed with acetone and a small quantity of methylc alcohol. In the first treatment by caustic alkali, the oils and acetone had been held in solution by the greater quantity of methyl-alcohol then present. The potash-solution was distilled, and the distillate, after desiccation, separated by chloride of calcium into methyl-alcohol and acetone, the latter being soluble in water, from which it was again separated by chloride of calcium or potash. The oils and acetone were separated by mixing with water, which dissolved the acetone, the oils separating out and floating on the surface. The acetone was precipitated from its aqueous solution by potash, and

thereby separated from a small quantity of methylic alcohol which had dissolved in it.

It appears from the preceding, that methylic alcohol and acetic acid are the principal substances contained in crude wood-spirit, acetone and oils being also present in comparatively small quantities. (Gould.)

Penta-iodide of Tetramethylum. $(C_2 H_3)_4 N, I_5$.—An alcoholic solution of iodine added to a heated solution of proto-iodide of tetramethylum, throws down the penta-iodide in an abundant crop of needles, having a metallic lustre.

					Weltzien.
8 C	48	6.82 6.89
N	14	1.99	
12 H	12	1.70 1.90
5 I	680	89.49 89.05 88.82
$C_8 N H_{12} I_5$					704 100.00

This compound is decomposed by boiling with water, yielding a yellow liquid, from which white, opaque, well-formed crystals of proto-iodide of tetramethylum, $C_2 N H_3 I$, separate; and on the other hand, still higher iodides are probably formed. The crystals of the proto-iodide yielded by analysis 23.72 p. c. C, 6.28 H, and 61.38 I; the formula requiring 24 p. c. C, 6 H, and 63 I. (Weltzien.)

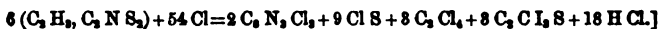
Deca-iodide of Tetramethylum. $(C_2 H_3)_4 N, I_{10}$.—On adding iodine to a boiling solution of the penta-iodide in dilute alcohol, there was formed at the bottom of the boiling liquid, a melted mass, which crystallised on cooling, and gave off iodine-vapors when exposed to the air.

					Weltzien.
8 C	48	8.60	
N	14	1.06	
12 H	12	0.90	
10 I	1260	94.44 95.85
$C_8 N H_{12} I_{10}$					1384 100.00

The compound ammoniums containing 4 At. Me, Ae, &c., whose compounds are not volatile, and whose hydrated oxides bear a close resemblance to potash, appear to be the only ones capable of forming these periodides. The solution of iodine in iodide of potassium may, perhaps, contain similar periodides of potassium. (Weltzien, *Ann. Pharm.* 91, 41.)

Action of Chlorine on Sulphocyanide of Methylene.—Dry chlorine attacks sulphocyanide of methylene in the cold, even under the influence of mere diffused daylight; but the action soon comes to an end. The product is a liquid having a faint yellow color, together with very beautiful colorless crystals of *solid chloride of cyanogen*. If the vessel be then exposed to direct sunshine, the quantity of

these crystals continually increases, and a very mobile liquid (a) is finally obtained, having a fine red color arising from *chloride of sulphur*, and containing a large quantity of crystals. This liquid begins to boil at 70°, but the last portions do not pass over below 200°. If the portion which distils over below 85° or 86° be shaken up with potash-ley, till the chloride of sulphur is completely decomposed, and the remaining liquid dried over fused chloride of calcium and distilled, a colorless aromatic distillate is obtained which boils at 80°, and exhibits the composition of *bichloride of carbon* $C_2 Cl_4$ (analysis: 7.99 p. c. C and 92.3 Cl). This compound appears to be a constant product of the action of chlorine on the sulphuretted compounds of the methyle series (pp. 500°—504°). The portion of the liquid (a) which passes over between 140° and 170°, shaken up with potash-ley, washed with pure water, then dried and carefully distilled, yields a very mobile amber-colored liquid, which boils between 150° and 160°, and exhibits the composition and properties of perchlorinated methylic sulphide, $C_2 Cl_4 S$.—[The formation of these several products may be represented by the following equation :



(A. Riche, *N. Ann. Chim. Phys.* 43, 295.)

Formation of Alcohol from Olefant Gas.—A large glass globe, capable of holding 81 or 32 litres, was exhausted of air and filled with olefant gas; 900 grammes of pure and boiled sulphuric acid, poured into it in several separate portions; then a few kilogrammes of mercury; and the whole submitted to violent and long-continued agitation: the gas was then gradually absorbed. After frequent agitations, the absorption became too slow, and the operation was discontinued; the quantity thus absorbed amounted to 30 litres. The acid was then mixed with 5 or 6 times its volume of distilled water; and, after repeated distillation, and subsequent separation by means of carbonate of potash, 52 grammes of hydrated alcohol were obtained, containing 45 grammes of absolute alcohol. This weight corresponds to $\frac{3}{4}$ of the olefant gas absorbed, the rest was lost in the several manipulations.

The alcohol thus obtained exhibited all the characters of ordinary alcohol, having a spirituous taste and odor, distilling without residue at 79° to 81°, yielding olefant gas, when heated with oil of vitriol, and acetic ether when heated with a mixture of acetic and sulphuric acids.

To obtain further confirmation of the result, olefant gas obtained by the action of hydrochloric acid and mercury on iodide of ethylene ($C_2 H_4 I_2 + 4 Hg = C_2 H_4 + 2 Hg_2 I_2$), was absorbed by oil of vitriol, and the liquid saturated with carbonate of baryta or lime; in this manner the sulphovicates of baryta and lime were obtained.

The baryta-salt distilled with an acetate of soda, yielded acetic ether; with butyrate of potash, butyric ether; and with benzoate of potash, benzoic ether. This last product boiled at 210° , and when treated with potash, was resolved into benzoic acid and alcohol.

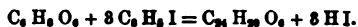
Lastly, to show that the same results may be obtained with olefiant gas not originally derived from alcohol, coal-gas was subjected to the action of iodine, and the resulting iodide of ethylene decomposed by heating it with potash. The pure olefiant gas thus obtained was absorbed by sulphuric acid as before, and by the series of operations just described, benzoic ether was obtained, which, when distilled with potash, yielded benzoic acid and alcohol. (Berthelot, *N. Ann. Chim. Phys.* 43, 385.)

Preparation of Chloride of Ethylene.—A tubulated retort is half filled with a mixture of 2 pts. peroxide of manganese, 3 pts. common salt, 4 pts. water, and 5 pts. oil of vitriol, and loosely connected with a flask, to serve as a receiver. Olefiant gas is then passed into the mixture by means of a tube passing through the cork of the tubulure and dipping half an inch below the surface of the liquid. So long as the gas is passing through the mixture, the retort must be only very gently heated,—as by placing a single red-hot coal under it—and the resulting chloride of ethylene afterwards distilled off at a higher temperature. If this precaution be attended to, the operator will not be annoyed by escape of chlorine. Coal-gas, if at hand, may be used as the source of the ethylene; if not, the gas may be prepared from alcohol by Wöhler's method. The crude product thus obtained in an hour and a half from 2 ounces of alcohol, yielded 1 ounce of pure chloride of ethylene. (H. Limpricht, *Ann. Pharm.* 94, 243; *Chem. Soc. Qu. J.* 8, 157.)

The Compound Ethers.—Cahours and Hofmann, by treating iodide of acryle with various silver-salts, have obtained a number of acryle-salts or compound ethers, and in particular the oxalate of acryle, a liquid which is decomposed by ammonia in a similar manner to oxalate of ethyle, yielding oxamide and *Acrylic alcohol*, $C_3H_5O_2$, or $C_3H_5 \left\{ \begin{smallmatrix} H \\ H \end{smallmatrix} \right\} O_2$; and from this a large number of derivatives have been formed, viz., acrylic ether, sulphacrylic acid, xanthacrylate of potassium, &c., &c. (*Compt. rend.* 42, 217.)

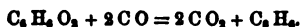
Berthelot and De Luca have also obtained several compound acrylic ethers, e. g. the butyrate, benzoate, &c., by the action of silver-salts on the iodide of acryle. They find, also, that the iodide, when decomposed by mercuric oxide, yields acrylic ether C_3H_5O ; treated with potash dissolved in vinic or amylic alcohol, it yields vinacrylic ether, $C_3H_5 \left\{ \begin{smallmatrix} C_6H_5 \\ C_6H_5 \end{smallmatrix} \right\} O$, or amylacrylic ether, $C_3H_5 \left\{ \begin{smallmatrix} C_{10}H_{21} \\ C_{10}H_{21} \end{smallmatrix} \right\} O$; and with potash and glycerine, it forms *triacryline*, $C_{30}H_{50}O_6 =$

$C_3 \left\{ \begin{smallmatrix} H_1 \\ (C_1 H_1)_1 \end{smallmatrix} \right\} O_1$. This last reaction is represented by the equation:



Iodide of acryle decomposed by sodium, yields the radical *acryle* $C_3 H_5$, which is a very volatile liquid, having a pungent odor like that of horse-radish. It boils at 59° . Its density is 0.684 at 14. Vapor-density = 2.92 (monatomic). Burns with a very bright flame. (*Compt. rend.* 42, 233.)

Propylene.—When a mixture of an alkaline acetate and oxalate is distilled in such a manner as to place the resulting acetone, when in the nascent state, in contact with carbonic oxide, the acetone is deoxidised, with formation of a carbonate and evolution of propylene.



The quantity of propylene obtained is, however, by no means equal to that which is indicated by calculation: for the decomposition of the two salts is not simultaneous, and the oily matter observed in the preparation of acetone is always produced. The mode of conducting the process is as follows: 1 At. acetate of lime is added to 1 At. oxalate of potash dissolved in water, so as to form oxalate of lime and acetate of potash; the liquid evaporated and constantly stirred, so as to obtain an intimate mixture; and the mass, when dried as completely as possible, put into a retort which is heated over a moderate fire. The gas passes first into a flask filled with carded cotton, then into another containing oil of vitriol to absorb the oily matter, and is finally condensed in bromine, after being washed with water. A kilogramme of acetate of lime thus treated yields about 60 grms. of crude propylene. The liquid thus obtained is washed with potash and distilled; then shaken up again with an alkaline solution, to saturate the hydrobromic acid formed during the distillation; after which it is dried over chloride of calcium and rectified. Bromide of propylene, $C_3 H_5 Br$, forms about two-thirds of the product; it has the odor and the boiling point (145°) of the bromide of propylene obtained from amylic alcohol.

The compound $C_3 H_5 Br$, obtained by the action of alcoholic potash on the preceding product, heated in a tube with sulphocyanide of potassium, yields oil of mustard. (L. Dusart, *Compt. rend.* 41, 495.)

Propylene is also found among the products of the dry distillation of butyrate of baryta. When the gas evolved in that process was passed into a mixture of hydrochloric acid and peroxide of manganese, and that mixture afterwards distilled, a distillate was obtained consisting of chlorinated substitution products of propylal and propione, mixed with chloride of propylene. The excess of chlorine was removed by washing with water, the liquid then dried

over chloride of calcium and rectified. The whole of the chloride of propylene passed over below 120° , and was obtained sufficiently pure for analysis when the boiling-point was between 104° and 110° , and the vapor no longer excited tears, a property possessed in a high degree by chlorinated propylal or propione. The chloride of propylene thus purified gave by analysis 61.86 p. c. chlorine, the formula C_3H_5Cl , requiring 62.51 p. c.—500 grms. of butyrate of baryta yielded 1 grm. of chloride of propylene. (Limpricht and v. Usler, *Ann. Pharm.* 94, 329.)

Formation of Propylic Alcohol from Propylene.—Oil of vitriol rapidly absorbs propylene gas; and on subsequently diluting the acid with water, filtering, and distilling, propylic alcohol is obtained in the form of a spirituous liquid, having a peculiar pungent odor, soluble in water, but precipitated from the solution by carbonate of potash. In a state of concentration, but still mixed with a certain quantity of water, it has a density of 0.817, and begins to boil at 81° or 82° , [the pure alcohol boils at 96°]. It mixes in all proportions with water, and forms with crystallised chloride of calcium, either a homogeneous solution or two distinct strata, according to the proportion of the salt. Burns with a brighter flame than common alcohol. Heated with oil of vitriol and sand, it blackens, decomposes rapidly, and yields propylene-gas, mixed with about $\frac{1}{10}$ of another combustible gas, probably hydride of propyle, C_3H_4 . Distilled with oil of vitriol and butyric acid, it yields *butyrate of propyle*, $C_3H_7(C_4H_7)O_2$, which is a neutral liquid, lighter than water, volatile below 130° , and having an odor like that of butyric ether, but not so agreeable; it is decomposed at 100° by potash, yielding butyrate of potash and propylic alcohol. Distilled with oil of vitriol and acetic acid, it yields acetate of propyle, $C_3H_7(C_2H_3)O_2$, which volatilises below 90° .

A mixture of propylic alcohol and oil of vitriol, gently heated, and then saturated with carbonate of baryta, yields sulphopropylate of baryta $C_3H_7BaO_2, 2SO_2 + 6Aq$. This salt parts with its water of crystallisation in vacuo. With benzoate of potash it yields benzoate of propyle. By immediately saturating with carbonate of baryta the solution of propylene in sulphuric acid, two salts were obtained, viz., $C_3H_7BaO_2, 2SO_2 + 6Aq$, identical with that just mentioned, and $C_3H_7BaO_2, 2SO_2 + 2Aq$, corresponding with the sulphovinate. These two hydrates exhibit the same degree of stability and behave in the same manner with various salts, both producing the acetate, butyrate, and benzoate of propyle. The compound formed with propylene and fuming oil of vitriol, does not reproduce these ethers.

Propylene is likewise absorbed by hydrochloric acid. When left to stand at ordinary temperatures over the fuming acid, it is slowly taken up, and disappears after some weeks, the absorption taking place even in a sealed tube. At 100° it is complete in 30 hours.

The product is a neutral liquid, lighter than water, and insoluble in that liquid. After being purified with potash and distilled, it consists for the most part of chloride of propyle, C_3H_7Cl , which volatilises at about 40° , and has the odor, taste, and flame of chloride of ethyl. (Berthelot, *N. Ann. Chim. Phys.* 43, 385; *Compt. rend.* 40, 102.)

Butyle.—According to recent experiments by Wurtz (*N. Ann. Chim. Phys.* 44, 275; *Ann. Pharm.* 96, 364), it appears that sodium may be used in the preparation of butyle with greater advantage than potassium, because it acts less violently on iodide of butyle, and does not form so large a quantity of gaseous secondary products. 100 pts. of iodide of butyle and 13 or 14 pts. of sodium are introduced into a flask provided with an upright condensing tube kept cool by ice-water. The action begins at ordinary temperatures, and with evolution of heat, the sodium swelling up and gradually becoming covered with a blue crust. As the action slackens, it must be accelerated by external heat, and the liquid kept boiling till the blue color of the sodium has disappeared, and the flask contains a white mass of iodide of sodium saturated with butyle. The butyle is then distilled from the flask, and the distillate rectified over sodium till the metal completely retains its lustre in the boiling liquid, and is no longer attacked. The portion which in the last rectification distils over between 105° and 108° , is pure butyle.

Butyle has a density of 0.7057 at 0° . It boils at 106° . Vapor-density = 4.070. None of the butyle compounds can be directly prepared from it. Chlorine and bromine act upon it, but form substitution-products. With perchloride of antimony, it yields hydrochloric acid and chlorinated products not yet examined. Pentachloride of phosphorus is decomposed by it only after long boiling, with formation of terchloride of phosphorus, chlorinated butyle, and hydrochloric acid. When the vapors of iodine and butyle are passed together over spungy platinum, heated in a tube to 300° , a large quantity of hydriodic acid is formed, together with a small quantity of an iodised organic substance, probably a substitution-product. Hydrochloric acid has no action upon butyle, either at ordinary temperatures or at a temperature near that of boiling oil. (Wurtz.)

Ethylbutyle.— $C_{11}H_{24} = \begin{matrix} C_4H_9 \\ C_7H_{15} \end{matrix}$. Obtained by decomposing 40 pts. of iodide of butyle and 34 pts. of iodide of ethyle with 11 pts. of sodium, as in the preparation of butyle. The action begins spontaneously, but requires external heat to keep it up; and the boiling must be continued till the sodium is converted into a white mass. On subsequently distilling the contents of the flask in the oil-bath, the thermometer remains stationary for some time between 60° and 70° . The portion which passes over at below 100° must be col-

lected apart (between 100° and 110° a considerable quantity of butyle distils over), heated with sodium in a sealed glass tube, and redistilled as soon as the fused sodium immersed in it retains its metallic lustre. The thermometer then remains nearly constant between 60° and 65° ; and by a second rectification of the portion which distils over between these temperatures, the ethylobutyle is obtained in the pure state.

Transparent, very mobile liquid, of sp. gr. 0.7011 at 0° . Boils at 62° . Vapor-density = 3.053.

12 C	72	88.72	88.43
14 H	14	16.28	16.50
$C_{12}H_{14}$	86	100.00	99.98
C-vapor	Vol. 12	Density. 4.9990	
H-gas	14	0.9702	
Vap. of $C_{12}H_{14}$	2	5.9622	
	1	2.9811	

Ethyl-amyle, C_4H_9 , and *Butyl-amyle*, C_3H_7 , are prepared by exactly similar processes; *Butyl-caproyle*, C_3H_7 , by the electrolysis of a mixture of valerate and cenantylate of potash; and *Methyl-caproyle*, C_3H_7 , by the electrolysis of a mixture of acetate and cenantylate of potash.

Radical.	Formula.	Sp. gr. at 0° .	Vapor-density.		Boiling Point.
			Observed.	Calculated.	
Ethyl-butyle.....	$C_{12}H_{14} = C_4H_9$	0.7011	3.053	2.972	62°
Ethyl-amyle	$C_{14}H_{16} = C_4H_9$	0.7069	3.522	3.455	68
Methyl-caproyle ?	$C_{14}H_{16} = C_4H_9$?	3.426	3.455	82?
Butyle	$C_{16}H_{18} = C_4H_9$	0.7057	4.070	3.989	104
Butyl-amyle	$C_{18}H_{20} = C_4H_9$	0.7247	4.465	4.423	132
Amyle.....	$C_{20}H_{22} = C_4H_9$	0.7413	4.956	4.907	158
Butyl-caproyle	$C_{22}H_{24} = C_4H_9$?	4.917	4.907	155
Caproyle.....	$C_{24}H_{26} = C_4H_9$	0.7574	5.983	5.874	202?

The mode of formation of these compound radicals, and a comparison of their properties with those of the simple radicals, affords an additional argument in favor of the theory which supposes the simple radicals, in the free state, to form diatomic vapors, regarding

methyle in the free state as C_2H_5 , ethyle as C_2H_5 , &c. In fact, on comparing the physical properties of the simple and compound radicals, as exhibited in the preceding table, it is plainly seen that they are members of the same series, and that, to establish a regular connection between the properties of these bodies and their formulæ, it is absolutely necessary to double the formulæ of the simple radicals. (Wurtz.)

Schweinfurt Green and Butyric acid.—When butyric acid is saturated with recently precipitated carbonate of copper, and the solution mixed with a solution of arsenious acid saturated at a boiling heat, a yellowish-green amorphous precipitate is formed, which, after a while, becomes crystalline, and exhibits the fine green color belonging to ordinary Schweinfurt green, which it also resembles in its other properties. (Wöhler, *Ann. Pharm.* 94, 44.)

					Springmann.
3 Cu O	120	80.2	80.5
3 As O ₃	198	49.9	50.1
C ₂ H ₃ O ₂	79	19.9	19.4
<hr/> 2 (Cu O, As O ₃) + C ₂ H ₃ Cu O					<hr/>
	897	100.0	100.0

This salt differs therefore in stoichiometrical composition from the true Schweinfurt green, the latter containing 3 At. arsenite of copper to 1 At. acetate.

Alloxanic acid.—To obtain alloxantin from the mother-liquor which remains in the preparation of alloxan by the action of nitric acid upon uric acid, Schlieper recommends that the excess of acid be neutralised with chalk before passing sulphuretted hydrogen through the liquid, in order to prevent oxidising action. With due care not to add too much chalk, this process succeeds well enough; but if the nitric acid be completely neutralised with chalk, bicarbonate of lime is formed at the same time, and rapidly converts the alloxan into alloxanic acid.

This process may be advantageously applied to the preparation of alloxanic acid. If the dilute acid mother-liquor be mixed with excess of chalk, said alloxanate of lime immediately separates, partly on the surface of the liquid, partly as a precipitate, in well-defined crystals or crystalline crusts, which may be easily freed from admixed chalk by elutriation. It is best to add a considerable excess of chalk and to stir frequently; the salt then forms and separates out very quickly. The heavy crystals remaining after the elutriation may be purified by dissolving them in water, not quite at a boiling heat, and filtering while still hot; the alloxanate of lime is then deposited in white crusts as the liquid cools. Extremely beautiful crystals are often found in the scum which forms when the mother-liquor of alloxan is saturated with chalk. These crystals are perfectly transparent, glassy, oblique six-sided prisms, but

generally having two of their faces so little developed, that they appear like acute rhombohedrons. In dry air, they very soon give off a portion of their water of crystallisation, and become milk-white.

<i>Milk-white crystals dried over oil of vitriol.</i>				Städeler.
Ca O.....	28	12.50 12.59
8 C.....	48	21.43 21.12
2 N.....	28	12.50 12.72
8 H.....	8	8.57 8.63
14 O.....	112	50.00 49.94
<hr/> C ₈ N ₂ H ₈ Ca O ₁₀ + 5 Aq.....				224 100.00 100.00

Or:

				Städeler.
Ca O.....	28	12.50 12.59
C ₈ N ₂ H ₈ O ₈	151	67.41
5 H O.....	45	20.09 19.70
<hr/> C ₈ N ₂ H ₈ Ca O ₁₀ + 5 Aq.				224 100.00

This is the composition which Schlieper assigns to the transparent, air-dried salt; but according to Städeler, the transparent crystals contain 1 At. water more, their composition being C₈ N₂ H₈ Ca O₁₀ + 6 Aq. When dried over oil of vitriol, they give off 3.86 p. c. water; calculation for 1 At. requiring 4.25 p. c. When acid alloxanate of lime crystallises from a solution saturated while warm, the crystals are not perfectly transparent, and contain between 5 and 6 At. water; when dried over oil of vitriol, they give off 2 to 3 p. c. water.

From the lime-salt, the *free acid* may be readily obtained as follows: The concentrated solution, supersaturated with ammonia, is precipitated by carbonate of ammonia; the liquid heated and filtered (in the cold the precipitation is imperfect); the filtered solution of the ammonia-salt left for a while over oil of vitriol to remove the free ammonia, and then precipitated with acetate of lead; the lead-salt, which is free from ammonia, suspended while yet moist, in alcohol, and decomposed by sulphuretted hydrogen; and the alcoholic solution of alloxanic acid evaporated at a gentle heat. The acid then remains in the form of a colorless viscid mass, which has a very sour taste, and gradually solidifies in the crystalline form. Schlieper (*Ann. Pharm.* 55, 259) is of opinion that the amorphous state is brought about by the application of too much heat during the evaporation; but the observation just quoted shows that the acid at first assumes the amorphous state when the alcoholic solution is evaporated over oil of vitriol at ordinary temperatures. (G. Städeler, *Ann. Pharm.* 97, 120.)

INDEX.

	PAGE		PAGE
INTRODUCTORY.....	11	Tables illustrative of these Bases and their Radicals.....	43, 45
Elements constituting the Organic world.....	11	The existence of these Bases illustrates the nature of the Vegetable Alkalies.....	46
These are nearly the same as those forming the chief mass of the Mineral world, except in the order of their relative abundance.....	12	II. CARBONIC OXIDE as a Radical, or OXALYLE.....	47
Distinctions between Organic and Inorganic Compounds.....	18	Its compounds:	
The Vital Force modifies Chemical Attraction.....	18	a. With Oxygen; Oxalic acid.....	47
Carbon predominates in Organic Compounds.....	14	Oxalates.....	48
General Observations on Compound Radicals.....	15	b. With Amide; Oxamide.....	49
Use of the Assumption of these.....	18	Oxamic acid.....	49
Curious Series of Volatile Oily Acids of Analogous Constitution.....	19	c. With Chlorine: Phosgene Gas.....	50
Theory of Types, and Doctrine of Substitutions.....	20	Carbamide.....	51
In Compound Molecules, the Position of the Elementary Molecules is of great importance.....	23	d. With Potassium, or Hydrogen and Oxygen.....	51
Decompositions and Metamorphoses of Organic Compounds.....	25	Rhodizonic Acid.....	51
1. Oxidation:		Croconic Acid.....	51
a. Direct.....	26	Mellitic Acid.....	52
Combustion.....	27	Mellitate of Ammonia.....	52
Eremacausis.....	28	Action of Heat on that Salt.....	52
b. Indirect.....	28	Euchronic Acid and Parmide.....	52
2. Action of Acids.....	29	III. CYANOGEN.....	53
a. Of Nitric Acid.....	29	Its Compounds:	
b. Of Sulphuric Acid.....	29	a. With Hydrogen: Hydrocyanic Acid, Anhydrous.....	55
c. Of Phosphoric Acid.....	30	Medicinal.....	55
d. Of Hydrochloric Acid, &c.....	30	b. With Oxygen.....	59
3. Action of Bases.....	30	Cyanic Acid.....	59
4. Action of Heat, or the Destructive Distillation.....	31	Cynates.....	59
5. Action of Ferments.....	33	Cynate of Ammonia.....	59
Theories of Fermentation.....	33	(Urea).....	60
Different kinds of Fermentation.....	34	Artificial Urea.....	60
Putrefaction.....	34	Compounds of Urea with Acids.....	62
It pertains to Eremacausis.....	35	Fulminic Acid.....	62
Action of certain Poisons and Miasmata.....	36	Fulminating Mercury and Fulminating Silver.....	62
Putrefaction or Spontaneous Decomposition of the Aqueous Solution of Cyanogen.....	36	Cyanuric Acid.....	63
General Views concerning the Organic Acids.....	37	Cyanurates.....	64
Arrangement of the Subject.....	39	Cyanamide.....	64
COMPOUND RADICALS KNOWN OR ADMITTED.		Constitution of the three preceding Acids.....	65
I. AMIDE OR AMIDOGEN.....	40	a. With Nitrogen: Mellone.....	66
Its Compounds:		d. With Chlorine.....	66
a. With Hydrogen, Ammonia, Ammonium, &c.....	41	e. With Bromine, Iodine, and Sulphur.....	66
Ammonia always present in the Atmosphere.....	41	f. With Metals.....	67
b. With Metals.....	42	Cyanides.....	67
a. With Platinum; new Bases of Gros and Reiset.....	42	Double Cyanides.....	68
		IV. FERROCYANOGEN.....	69
		Its Compounds:	
		a. With Hydrogen: Ferrocyanic Acid.....	69
		b. With Metals: Ferrocyanides.....	70
		Ferrocyanide of Potassium.....	70
		of Iron.....	71
		V. FERRIDCYANOGEN.....	72
		Its Compounds:	
		a. With Hydrogen: Ferridcyanic Acid.....	72
		b. With Metals.....	72
		Ferridcyanide of Potassium.....	72
		VI. COBALTOCYANOGEN.....	74
		Its Compounds with Hydrogen and Potassium.....	74

	PAGE		PAGE
VII. CHROMOCYANOGEN.....	75	1. Uric Oxide, or Xanthic Oxide....	101
VIII. PLATINOCYANOGEN.....	75	2. Cystic Oxide.....	101
Platinocyanide of Potassium.....	75	3. Guanine.....	101
IX. IRIDI-CYANOGEN.....	75	4. Hyperuric Acid.....	102
Iridiocyanide of Potassium.....	76	XIII. BENZOYLE.....	102
Palladiocyanogen and Manganocyanogen.....	76	Its Compounds:	
Observations on the eight preceding Radicals.....	77	a. With Oxygen: 1. Benzole Acid....	102
Paracyanogen.....	77	b. With Hydrogen: 2. Hyduret of Benzoyl.....	102
X. SULPHOCYANOGEN.....	77	c. With Chlorine: 3. Chloride of Benzoyl.....	104
Its Compounds:		d. With Amide: 4. Benzamide.....	104
a. With Hydrogen, Hydrosulphocyanic Acid.....	77	5. Formobenzollic Acid.....	105
b. With Potassium and other Metals.....	78	6. Benzate of Hyduret of Benzoyl.....	105
Hydroperasulphocyanic Acid.....	79	7. Hippuric Acid.....	105
Action of Heat on Sulphocyanide of Potassium.....	79	Products of its Decomposition.....	106
XI. MELLONE.....	79	Products derived from the Compounds of Benzoyl.....	107
Its Compounds:		1. Hyposulphobenzole Acid.....	107
a. With Hydrogen: Hydromellonic Acid.....	80	2. Bromobenzole Acid.....	107
b. With Potassium and other Metals.....	80	3. Benzole.....	107
Products of the Distillation of Sulphocyanide of Ammonium.....	81	Its Derivatives:	
Melam.....	81	4. Sulphobenzide.....	107
Melamine and Ammeline.....	82	5. Hyposulphobenzidic Acid.....	108
Ammeline.....	82	6. Nitrobenzide or Nitrobenzole....	108
Tabular View of these Products, and of their Relation to Cyanuric Acid.....	83	Aniline.....	108
New Analogous Product derived from Urea.....	88	Dinitrobenzole.....	108
Action of Nitric Acid on Mellone; Cyanlic Acid.....	84	Nitraniline.....	108
Sulphomellone.....	85	7. Azobenzide.....	108
Hydrosulphomellonic Acid.....	85	8. Chloride of Benzole.....	108
Sulphomellonides.....	85	9. Chlorobenzine.....	108
CYANOGEN WITH CARBONIC OXIDE (OXYL) OR		10. Benzene.....	109
XII. URYLE.....	86	11. Hydrobenzamide.....	109
Uric Acid.....	86	12. Benzhydramide.....	109
Products of its Oxidation:		13. Azobenzoyl.....	109
a. By Peroxide of Lead.....	88	14. Azotide of Benzoyl.....	109
Allantoin.....	88	15. Benzostilbene.....	109
b. By Peroxide of Manganese.....	89	16. Benzolone.....	110
a. By Permanganate of Potash.....	89	17. Amarine.....	110
d. By Nitric Acid.....	89	18. Lophine.....	110
1. Alloxan.....	89	19. Benzimide.....	111
Derivatives of Alloxan.....	90	20. Benzoin.....	111
2. Alloxanic Acid.....	91	21. Hydrobenzoinamide.....	111
3. Leucoturic Acid.....	92	22. Benzoinam.....	112
4. Difuran.....	92	23. Benzile.....	112
5. Hydruillic Acid.....	93	24. Benzilic Acid.....	112
Nitrohydruillic Acid.....	93	25. Azobenzolide.....	112
6. Mesoxalic Acid.....	98	26. Cyanobenzile.....	112
7. Mycomellinic Acid.....	94	27. Hyduret of Sulphobenzoyl.....	112
8. Parabanic Acid.....	94	28. Stilbene.....	112
9. Oxaluric Acid.....	94	Sulphesale.....	112
Oxalurate of Ammonia.....	95	Chloride of Stilbene.....	112
10. Thionuric Acid.....	95	Chlostilbase.....	112
Thionurate of Ammonia.....	95	Bromides of Chlostilbase.....	112
11. Uramille.....	96	Chloride of Chlostilbase.....	112
12. Uramillic Acid.....	96	Bromide of Stilbene.....	114
13. Alloxantine.....	96	Nitrostilbase, &c.....	114
Derivatives of Alloxantine:		29. Hyduret of Sulphazobenzoyl.....	114
14. Dialuric Acid.....	97	30. Nitrobenzole Acid.....	114
15. Allitric Acid.....	98	31. Bromide of Benzole.....	114
16. Dilituric Acid.....	98	Bromobenziline.....	114
17. Murexide.....	98	32. Hydrocyanate of Benzoin.....	114
18. Murexan.....	100	33. Hydrocyanate of Benzile.....	114
Tabular view of some of the Compounds of Uryle.....	101	General remarks on the preceding compounds.....	114
Appendix to Uric Acid.....	101	Appendix to Benzoyl.....	116
		1. Amygdaline.....	116
		2. Amygdalinic Acid.....	116
		3. Distilled Water of Bitter Almonds.....	117
		4. Laurel Water.....	117
		Theory of the Formation of the Oil of Bitter Almonds.....	117
		Emulsine or Synaptase.....	117

	PAGE		PAGE
Mixture recommended by Liebig and Wohler instead of the distilled Water of Bitter Almonds or of Laurel.....	119	14. Oxalate.....	139
XIV. SALICYLE.	119	Oxalovinic Acid.....	140
Its Compounds:		15. Oxamate (Oxamethane).....	140
a. With Hydrogen: 1. Hyduret of Salicyle or Salicylous Acid.....	120	16. Sulphocarbonate of Oxide of Ethyle and Water: Xanthic Acid.....	140
Salicylurets or Salicylites.....	120	17. Allophanate.....	140
Salicylimide.....	120	Allophanic Acid.....	140
Melanic Acid.....	120	18. Benzoate.....	141
Parasalicyle.....	121	19. Hippurate.....	141
A new Product of the Action of Heat on Benzoate of Copper, possibly the Radical Benzoyle.....	121	20. Salicylate.....	141
b. With Oxygen: 2. Salicylic Acid.....	121	Anilate.....	141
Derivatives of Salicylic Acid:		Anilamide.....	141
Anilic Acid.....	122	Bromurated Salicylic Ether.....	142
Picric Acid.....	122	Compounds of Ethyle of uncertain constitution.....	142
Carbolic Acid.....	122	Chlorocarbonic Ether.....	142
c. With Chlorine: 3. Chlorosalicylic Acid.....	122	Urethane or Carbonic Ether.....	142
Chlorosalicylamide.....	122	Metamorphoses of the Compounds of Ethyle.....	142
d. With Nitric Acid: 4. Nitrosalicylic (Anilic) Acid.....	122	Oil of Wine.....	142
Appendix to Salicyle:		Heavy Oil of Wine.....	142
5. Salicine.....	122	Etherole.....	142
6. Saligenine.....	122	Etherine.....	142
Chlorosalicine, &c.....	124	Ethionic, Isethionic, Methionic and Althionic Acids.....	142
Chlorosaligenine, &c.....	125	Products of the Oxidation of Ethyle and its Derivatives.....	144
7. Saliretine.....	125	XVIII. ACETYLE.	144
8. Helicine.....	125	1. Hydrated Oxide of Acetyle or Aldehyde.....	145
Helicoidine.....	125	Aldehydammonia.....	146
Chlorohelicine, &c.....	125	Thialdine and Selenaldine.....	146
Rutiline.....	126	2. Acetal.....	147
9. Phloridrine.....	126	Elaldehyde.....	147
Phloretine.....	126	Metaldehyde.....	147
Phloridzeline.....	126	3. Aldehydic or Acetylous Acid.....	147
XV. CINNAMYLE.	126	4. Acetic or Acetylic Acid.....	147
Its Compounds:		Acetates.....	150
a. With Hydrogen: Hyduret of Cinnamyle.....	126	Action of Chlorine, Bromine, &c. on Ethyle, Acetyle, and their derivatives.....	152
b. With Oxygen: Cinnamic Acid.....	127	1. On Oxide of Ethyle.....	152
Nitrocinnamic Acid.....	127	2. On Salts of Oxide of Ethyle.....	152
Sulphocinnamic Acid.....	127	3. On Alcohol.....	153
Chlorocinnose.....	127	Chloral.....	155
Balsam of Peru.....	128	4. On Acetic Acid.....	155
Cinnametine.....	128	Chloroacetic Acid.....	155
Peruvine.....	128	5. On Sulphide of Ethyle.....	156
Balsam of Tolu.....	128	Bromal.....	156
Tolene.....	128	Compounds derived from Alcohol of uncertain constitution.....	156
Toluole or Benzoeene.....	128	Olefant Gas on Hyduret of Acetyle.....	156
XVI. GUAIACYLE.	128	Oil of Olefant Gas.....	157
Hyduret of Guaiacyle.....	128	Chloride of Acetyle.....	157
General Remarks on the Com. Radicals previously described.....	129	Chlorethral.....	158
XVII. ETHYLE.	130	Sulphacetylic Acid.....	158
Its Compounds:		Action of Bichloride of Platinum on Alcohol.....	158
a. With Oxygen: 1. Oxide of Ethyle.....	131	Action of Heat on Acetic Acid and the Acetates.....	159
2. Hydrated Oxide or Alcohol.....	133	Acetone.....	159
b. With Chlorine: 3. Chloride of Ethyle.....	135	Mesityl ?.....	159
4. Bromide of Ethyle.....	135	Mesitylene.....	160
5. Iodide of Ethyle.....	135	Pteyle.....	160
6. Sulphide of Ethyle.....	135	Compounds containing Arsenic derived from Acetyle.....	160
Hydrosulphide of Sulphide of Ethyle, or Mercaptan.....	135	XIX. CAODYLE.	160
Selenide and Cyanide of Ethyle.....	136	Its Compounds:	
7. Salts of Oxide of Ethyle.....	136	a. With Oxygen: Oxide of Caodyle.....	161
8. Acid Sulphate.....	137	Caodylic Acid.....	161
9. Acid Phosphate.....	138	b. With Chlorine, Bromine, Iodine, Sulphur, Cyanogen, &c.....	161
10. Nitrate.....	138	Compounds derived from Caodyle, and containing Platinum.....	162
11. Hyponitrite.....	138		
12. Carbonate.....	139		
13. Carbonate of Ethyle and Potash.....	139		

	PAGE		PAGE
Kakoplstyle.....	162	4. Malic Acid.....	194
Tabular view of its Compounds.....	162	Malates.....	195
Appendix to Ethyle and Acetyle: Sugar.....	163	Action of heat on Malic Acid.....	195
1. Cane Sugar.....	163	Maleic Acid.....	195
2. Grape Sugar.....	164	Paramaleic or Fumaric Acid.....	195
Sacchulmine and Sacchulmic Acid.....	166	5. Tannic Acid.....	196
Glucic and Melassic Acids.....	166	Tannates.....	197
Caramel.....	166	6. Gallic Acid.....	197
Metacetone and Metacetic Acid.....	166	Gallates.....	198
Action of Nitric Acid on Sugar.....	167	Transformations of Tannic and Gallic	
Saccharic Acid.....	167	Acids.....	198
3. Sugar of Milk or Lactine.....	168	Pyrogallie Acid.....	198
Mucic Acid.....	168	Metagallic Acid.....	198
Modified Mucic Acid.....	168	Ellagic Acid.....	198
Pyromucic Acid.....	169	Catechu: Mimotannic Acid.....	199
4. Sugar of Mushrooms.....	169	Catechine, or Tanningenic Acid.....	199
Vinous or Alcoholic Fermentation.....	169	Japonic and Rubinic Acids.....	199
Lactic Fermentation.....	171	7. Meconic Acid.....	200
Viscous Fermentation.....	172	Meconates.....	201
Butyric Fermentation.....	172	8. Comenic Acid.....	201
Mannite.....	173	Pyromeconic Acid.....	202
Lactic Acid.....	173	9. Kinic Acid.....	202
anhydrous.....	174	Kinates.....	202
Lactates.....	174	Products of Decomposition of Kinic	
XX. METHYLE.....	174	Acid.....	202
a. Hydrated Oxide, or Pyroxilic Spirit.....	175	Kinone.....	202
b. Oxide of Methylene.....	175	Hydrokinone, green and white.....	202
c. Chloride, Iodide, &c.....	176	Tabular view of the Derivation of	
d. Salts of Oxide of Methylene.....	176	Kinic Acid.....	202
Sulphate.....	176	Volatile Oily Acids.....	202
Bisulphate.....	176	10. Butyric Acid.....	204
Nitrate.....	176	Butyrates.....	204
Oxalate.....	177	Butyramide.....	205
Benzoate.....	177	Butyryne.....	205
Acetate.....	177	Caproic, Caprylic, and Capric Acids.....	205
Salicylate, or Oil of Gaultheria.....	177	Vaccinic Acids.....	205
Urethylane.....	177	Genanthylic Acid.....	206
Sulphamethylane.....	178	Genanthole.....	206
Oxidation of Methylene.....	178	Tabular View of Genanthylic, Ace-	
XXI. FORMYLE.....	178	tic and Cetyllic Acids.....	206
Formic Acid.....	178	Pelargonic Acid.....	206
Formates.....	179	Hircic, Cevadic, Veratric, and	
Chloride, Bromide, Iodide, &c., of		Crotonic Acids.....	206
Formyle.....	179	11. Camphoric Acid.....	207
XXII. CERYLE.....	182	Anhydrous Camphoric Acid.....	207
Hydrated Oxide, or Ethal.....	182	Camphor.....	207
XXIII. AMYLE.....	182	Borneo Camphor.....	208
Hydrated Oxide, or Oil of Potato Spirit.....	182	Camphogen.....	208
Other Compounds of Amyle.....	183	Camphrone.....	208
Oxidation of Hydrated Oxide of Amyle.....	183	12. Valerianic Acid.....	208
Valerianic Acid.....	183	13. Anisic Acid.....	208
Amilene.....	184	Nitransic Acid.....	209
XXIV. GLYCERYLE.....	184	Anisole.....	209
Hydrated Oxide, or Glycerine.....	184	14. Genanthic Acid.....	209
Other Compounds of Glyceryle.....	184	Genanthic Ether.....	209
ORGANIC ACIDS, THE RADICALS OF WHICH		15. Roselle Acid.....	209
ARE NOT YET ASCERTAINED.		16. Cumic Acid.....	209
1. Citric Acid.....	184	Cumene.....	210
Citrates.....	185	Cuminole.....	210
Action of Heat on Citric Acid.....	187	Cymene.....	210
Aconitic Acid.....	187	Cumyle, Hyduret of Cumyle, &c.....	210
Itaconic Acid.....	188	17. Eugenic Acid.....	210
Citraconic Acid.....	188	Caryophylline and Eugenine.....	210
2. Tartaric Acid.....	188	18. Cocinic Acid.....	210
Tartrates.....	189	19. Myristic Acid.....	211
Tartar Emetic.....	190	Myristine.....	211
Action of Heat on Tartaric Acid.....	191	20. Palmitic Acid.....	211
Tartrellic Acid.....	191	Palmitine.....	211
Tartrellic Acid.....	192	21. Cetyllic Acid.....	212
Anhydrous Tartaric Acid.....	192	22. Margaric Acid.....	212
Pyrotartaric Acid.....	192	Margarine.....	212
3. Rascenic Acid.....	192	Margarates.....	212
Rascenates.....	193	23. Stearic Acid.....	212

	PAGE		PAGE
Stearates.....	214	Oil of Mustard and its Derivatives.....	228
Stearine.....	214	Thiosinamine, Sinamine, Sinapoline, Myrosine, Sinapsine.....	228
Action of Nitric Acid on Stearic Acid.....	214	Allyle, the Radical of Oil of Mustard.....	229
Connection of Stearic and Margaric Acids.....	214	Oils of Garlic, Asafoetida, Horseradish, &c., also containing Allyle.....	230
Action of Nitric Acid on Margaric Acid.....	215	Compounds of Allyle.....	230
24. Suberic Acid.....	215	Concrete Volatile Principles allied to the Volatile Oils.....	230
Suberyle.....	215	Hellenine.....	230
25. Succinic Acid.....	215	Asarone.....	230
Succinates.....	216	Anemonine.....	231
Amber.....	216	Cantharidine.....	231
26. Oleic Acid.....	216	Caoutchouc.....	231
Oleates.....	217	Action of Heat on it.....	231
Oleine.....	217	Caoutchine.....	231
Action of Heat on Oleic Acid.....	217	Resins.....	231
27. Sebacic Acid.....	217	Turpentine and Colophony.....	232
Action of Nitrous Acid on Oleic Acid.....	217	Pinic and Sylvic Acids.....	232
28. Elaidic Acid.....	217	Resins of Copaiva, Elemé, Benzoin, Balsam of Tolu, &c.....	232
Elaidine.....	217	Benzoe or Toluole.....	232
Action of Nitric Acid on Oleic Acid.....	218	Nitrotoluole.....	232
Pimelic Acid.....	218	Binrotoluole.....	232
Adipic Acid.....	218	Styrax, Styracine.....	232
Lipic Acid.....	218	Styrole.....	232
Azoleic Acid.....	218	Metastyrole.....	232
Table of Nitric Volatile Acids formed along with the preceding.....	218	Nitrostyroles.....	232
Acids of Castor Oil.....	219	Resins of Gusiacum, Lac, Mastic, Dragon's-Blood, Sandersch, Jalap, Rhubarb, &c.....	233
Margaritic Acid.....	219	Chrysophanic Acid.....	233
Eicinic Acid.....	219	Copal.....	233
Action of Nitrous Acid on Castor Oil.....	219	Resins of Peat.....	233
Palmitic Acid.....	219	Resinous Varnishes.....	234
Palmine.....	219	Action of Heat on Resins.....	234
Natural Fats and Fixed Oils.....	220	Non-azotized Coloring Matters.....	234
Action of Heat on Fats and Fixed Oils:		1. Yellow.....	234
Acroleine.....	220	2. Red.....	235
Acryle.....	220	3. Blue.....	236
Acrylic Acid.....	220	4. Green: Chlorophyll.....	236
Oil Gas.....	221	Non-azotized Bitter and Crystalline Vegetable Principles.....	236
Action of Sulphuric Acid on Fat Oils.....	221	Azotized Coloring Matters and Allied Substances.....	239
Sulpholeic, Sulphomargaric, Metamargaric, Hydromargaritic, Metoleic, Hydroleic, and Hydromargaric Acids.....	221	1. Lecanoric Acid.....	240
Oleone and Elaeone.....	221	2. Lecanoric Ether.....	240
Action of Nitrous Acid and Nitrate of Mercury on Fat Oils.....	222	3. Orcine.....	240
Action of Bases on Fat Oils:		4. Paralleic Acid.....	240
Soaps and Plasters.....	222	5. Kryptic Acid.....	241
Vegetable Fats.....	223	6. Picroerythrine.....	242
Animal Fats:		7. Usnic Acid.....	242
Spermaceti.....	223	8. Chrysophanic Acid.....	242
Ambreine.....	224	9. Archil.....	242
Wax.....	224	10. Litmus and its Derivatives.....	242
Cerine.....	224	11. Phloridzeline.....	242
Myricine.....	224	12. Indigo.....	242
Cerosine.....	224	White or Reduced Indigo.....	244
Japan or Tree-Wax.....	224	Action of Sulphuric Acid on Indigo:	
Athamantine.....	224	Sulphoindigotic Acid, &c.....	246
Various Acids.....	224	Oxidation of Indigo.....	246
VOLATILE OILS.....	225	Isatine.....	246
1. Non-oxygenated.....	225	Isatinic Acid.....	247
Oil of Turpentine.....	225	Isatinosulphites.....	247
Dadyle and Peucyle.....	225	Chlorisatine.....	247
Oils of Juniper, Lemons, Savine, Copaiva, and other Non-oxygenated Oils.....	226	Chlorisatinic Acid.....	248
2. Oxygenated.....	226	Bichlorisatine.....	248
Oils of Cinnamon, Anise, Estragon, and other Oxygenated Oils.....	226	Bichlorisatinic Acid.....	248
Coumarine.....	227	Bromisatine, Bibromisatine, Bromisatinic Acid, &c.....	248
3. Sulphuretted.....	228		

	PAGE		PAGE
Tabular View	248	4. Xanthopenic Acid	266
Isatyde	249	4. Opianosulphurous Acid	266
Sulphesatyde	249	5. Sulphopanic Acid	266
Chlorisatyde	249	6. Hemipinic Acid	266
Bichlorisatyde	249	7. Cotarnine	266
Sulphasatyde	250	8. Humopinic Acid	267
Indine	250	9. Apophyllic Acid	267
Indine Acid	250	10. Narcogenine	267
Hydrindine	250	11. Narcotinic Acid	267
Nitrindine	250	Chelidonine	267
Chlorindine	250	Chelerythrine	267
Sulphistanous Acid	251	Glaucine	267
Isatan	251	Glaucopictine	267
Chlorindopten	251	d. Bases of the Solanaceæ, the Strychnaceæ, and other Vegetable Families	267
Chlorindatinit	251	Hyoscyamine	267
Chlorindoptenic Acid	251	Daturine	268
Trichloraniline	251	Stramonine	268
Chlorinized Chlorindoptenic Acid	251	Atropine	268
Chloraniline	252	Solanine	268
Chloranilic Acid	252	Veratrine	268
Chloranilammon	252	Sabadilline	269
Chloranilam	252	Colchicine	269
Action of Ammonia on Isatine	252	Aconitine	269
Imesatine	252	Delphine	270
Imasatine	252	Staphisine	270
Imasatinic Acid	252	Emetrine	270
Amasatine	252	Strychnine	270
Imechlorisatinase	252	Brucine	271
Imachlorisatinase	252	Jervine	271
Imabromisatinase	252	Various Bases	271
Action of Nitric Acid on Indigo and its Derivatives	252	Piperine	272
Anilic Acid	252	Theobromine	272
Picric Acid	252	Caffeine	272
Action of Potash on Indigo	254	a. Bases found in the animal body	274
Chrysanthilic Acid	254	Urea and Kreatinine	274
Anthranilic Acid	254	Other Bases, little known	274
Action of Heat on Anthranilic Acid	254	2. Artificial Organic Bases	274
Aniline	254	How obtained	275
Tabular View of the Series of Phenyle	255	Limits to our power of forming	
Derivatives of Aniline	256	Artificial Organic Products	276
Chloraniline	256	a. Volatile Oily Artificial Bases	276
Dichloraniline	256	Aniline	276
Trichloraniline	256	Derivatives of Aniline	276
Bromaniline, &c.	256	Oxanilide	276
Nitriline	256	Carbanilide	276
Tabular View of these Derivatives	256	Formanilide	276
Nitriline is a Base	257	Aniline Urea	276
Carmine and Cochineal	258	Analogy between Aniline and Ammonia illustrated in a Tabular View	279
Action of Nitric Acid on Aloes	258	Picoline	273
Chrysaminic Acid	258	Leucoline	278
Chrysopic Acid	259	Toluidine	279
ORGANIC BASES OR ALCALOIDS	259	Tabular view of the Natural and Artificial Oily Bases	279
1. Natural Alkaloids	260	b. Bases derived from Naphthaline	280
a. Liquid Volatile Bases	261	Seminaphthalidine	280
Nicotine	261	Naphthalidine	280
Cotinine	262	c. Bases from Oil of Mustard	280
b. Bases of Cinchona Bark	262	Thiosinamine	280
Quinine	262	Sinamine	280
Cinchonine	262	Sinapoline	280
Quinoidine	262	d. Bases derived from Aldehyde	280
Arcine	262	Thialdine	281
Other Analogous Bases	262	Selenaldine	281
a. Bases of the Papaveraceæ	262	e. Bases derived from Melan	281
Morphine	262	Tabular View of them	281
Codeine	264	f. Bases derived from Oil of Bitter Almonds	281
Thebaine	265	Amarine	281
Pseudomorphine	265	Lophine	281
Narceine	265		
Narcotine	265		
Derivatives of Narcotine:			
1. Opiatic Acid	266		
2. Opiammon	266		

	PAGE		PAGE
Picrine.....	292	Other Analogous Products.....	807
g. Base derived from Furfurole.....	293	2. Action of Sulphuric Acid on Naphthaline.....	810
Furfurine.....	293	Hyposulphonaphthalic Acid.....	810
A. Bases derived from Narcotine, Coptarnine, and Narcogenine.....	293	Hyposulphonaphthie Acid, &c.....	810
4. Bases derived from Animal Products.....	293	3. Action of Nitric Acid on Naphthaline and its Derivatives.....	810
Glycocoll.....	293	Nitronaphtase, Nitronaphtese, &c.....	811
Sarcosine.....	293	Naphtalase.....	811
Kreatinine.....	293	Nitronaphtale.....	811
General Views as to the Constitution of the Organic Bases.....	293	Nitronaphtesic Acid, &c.....	811
INDIFFERENT NON-AZOTIZED COMPOUNDS.....	296	Oxide of Chloroxenaphtose, &c.....	812
1. Starch.....	296	Phtallo Acid.....	812
Dextrine.....	297	Phtalamide and Phtalimide.....	812
Lelocoma.....	298	Nitrophthalic and Chlophthalic Acids, &c.....	312
Inuline.....	298	Anthracene.....	818
Lichenine.....	299	Tabular View of its Derivatives.....	818
2. Gum.....	299	Chrysene.....	818
Arabine.....	299	Pyrene.....	818
Mucilage.....	299	Ampeline.....	818
Bassorine.....	299	Ampelic Acid.....	818
Tragacanth.....	299	Fossil Resins, Wax, Oil, Naphtha, &c.....	814
Salep.....	299	Asphaltum.....	814
Cerasine.....	299	Petroleum.....	815
Pectine.....	299	Naphtha.....	815
Pectic Acid.....	299	Soot, Lamp-black, &c.....	315
Pectates.....	299	Sulphurized and Azotized Nutritious Compounds, Animal and Vegetable.....	815
Apline.....	291	Albuminous Substances.....	815
Glycyrrhizine.....	291	Theory of Proteins.....	815
Sarcocolline.....	291	Tabular View of Mulder's Formulae.....	815
3. Woody Fibre.....	291	The Proteine Theory is not at present tenable.....	815
Cellulose.....	291	1. Vegetable Albumen.....	817
Lignine.....	291	2. Vegetable Fibrine.....	817
Gun-Cotton.....	292	3. Vegetable Caseine.....	817
Erremaeausis or Decay of Wood.....	292	4. Emulsine or Synaptase.....	818
Humus, Humic Acid, &c.....	293	Fungine.....	818
Crenic Acid.....	293	Gladine.....	818
Apocrenic Acid.....	293	Diastase.....	819
Distillation of Wood.....	294	Malt.....	819
1. Volatile Products, soluble in water.....	294	Must. Beer, Ale, Porter, etc.....	820
Acetic Acid.....	294	Oil of Grain and of Potato Spirit.....	820
Pyroxylic Spirit.....	294	Panification.....	820
Lignone.....	294	Ferment, Yeast, Lees of Wine.....	821
Xylite.....	294	Caseous Oxide.....	821
Xylitic Oil, Resin, Naphtha, &c.....	294	5. Animal Albumen.....	822
Mesite.....	295	6. Animal Fibrine.....	822
2. Volatile Oily Products.....	295	7. Animal Caseine.....	824
Cresote.....	295	Milk.....	825
Picamar.....	297	Products of the decomposition of Caseine.....	825
Capnomor.....	298	Tyrosine and Leucine.....	826
Eupion.....	298	Action of Kennet on Milk.....	826
3. Solid Products.....	299	Composition of Milk.....	826
Paraffine.....	299	Cheese.....	826
Cedrine.....	299	Mucua, animal.....	827
Pittacal.....	299	8. Horny Matter.....	827
Pyroxanthine.....	299	Gelatinous tissues.....	827
Wood Coal, Brown Coal or Lignite.....	300	Gelatine or Glue.....	827
Distillation of Coal.....	300	Chondrine.....	827
a. Carbolic Acid.....	301	Products of the decomposition of Gelatine.....	827
Tabular View of Phenyle and its Derivatives.....	301	Valeronitrile and Valeracetoneitrile.....	828
b. Volatile Bases of Coal-Tar.....	302	Bones.....	828
Aniline, Picoline, and Leucoline.....	302	Bone Earth.....	828
c. Volatile Carbohydrogen in Coal-Tar.....	303	Bone-black.....	829
Naphthaline.....	303	The Bile.....	829
1. Action of Chlorine and Bromine on Naphthaline.....	304	Formula of pure Bile.....	829
Chlonaphtase.....	305	Choleic Acid.....	830
Bronaphtase.....	305	Cholestera.....	830
Chlonaphtese.....	305	Products of the Decomposition of Bile.....	831
Doctrine of Substitution applied to these Products.....	306		
Bronaphtase, Chlonaphtase, &c.....	307		

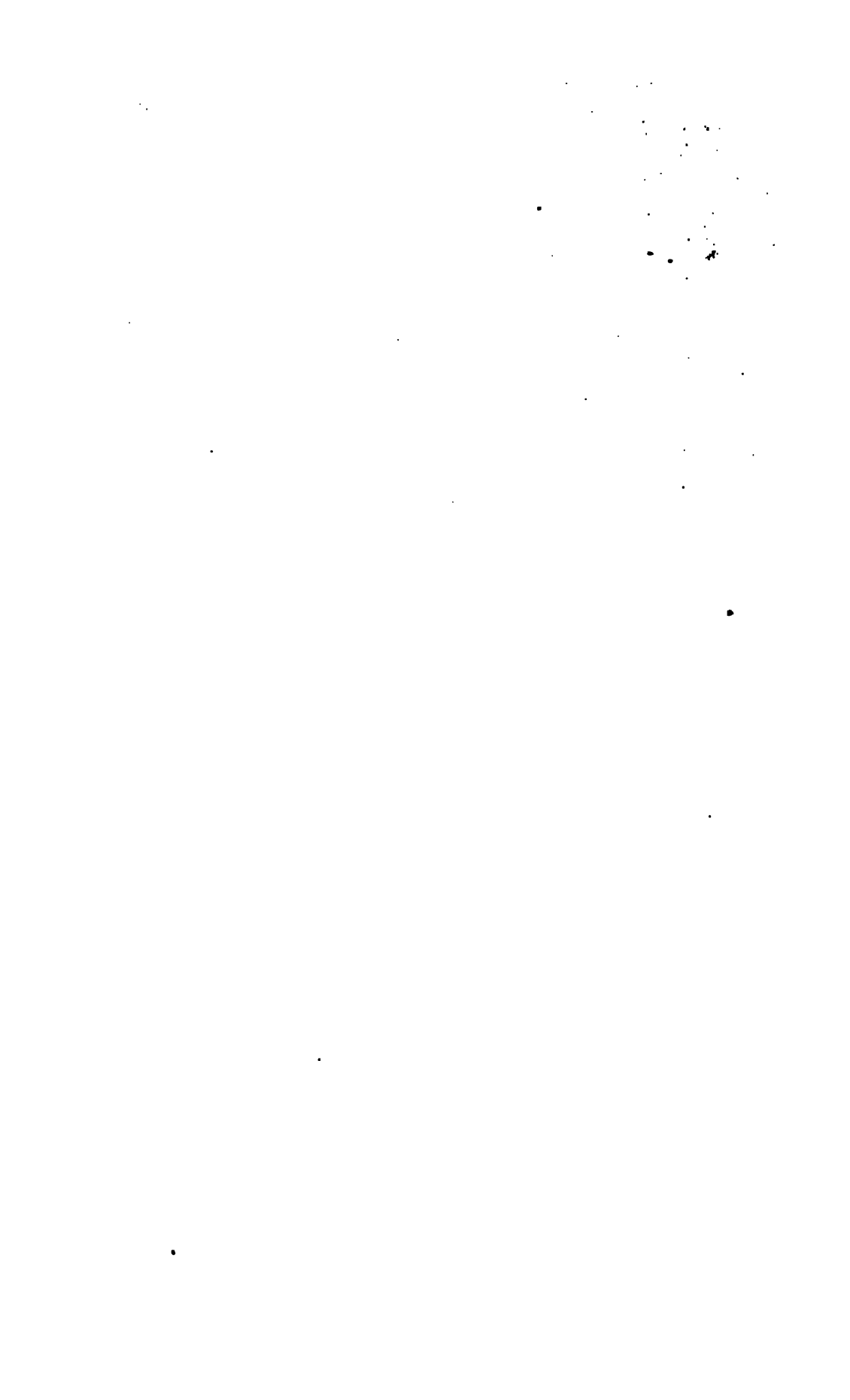
	PAGE		PAGE
1. Choloidic Acid	331	1. Vegetable Acids.....	339
Its Derivatives	331	2. Neutral Compounds.....	351
Choloidanic Acid.....	331	3. Neutral Bodies.....	351
Nitrocholic Acid.....	331	4. Volatile Oils and Aromatic Acids.....	353
Cholacrole.....	331	5. Oily and Fatty Acids.....	353
Cholesteric Acid.....	331	6. Resins and Camphors.....	353
2. Taurine.....	331	7. Carbohydriogens.....	354
3. Cholic Acid.....	331	Effect of Vegetation on the Air.....	354
4. Dyslysine.....	332	Sources of the Carbon in Plants.....	355
5. Cholic Acid of Gmelin.....	332	" " Nitrogen.....	354
6. Cholanic Acid.....	332	Ammonia in the Atmosphere.....	357
7. Felanic Acid.....	332	Transformations of Ammonia.....	358
Biliary Concretions.....	332	Formation of Amides.....	358
Lithofellic Acid.....	332	" " Imides and Nitryles.....	360
Cholesterine.....	332	Production of Nitrogenous Compounds.....	361
Brain and Nervous Matter.....	333	" " Albuminous or Sanguigenous Compounds.....	362
Cerebric Acid.....	333	Composition of Albumen, Caseine, and Fibrine.....	363
Oleophosphoric Acid.....	333	Vegetation a process of deoxidation.....	364
Cerebroleine.....	333	Mineral Food of Plants.....	365
Cholesterine.....	333	Sources of the Phosphates.....	366
Gastric Juice.....	334	Nature of Manures.....	367
Digestion.....	334	Farm-yard Manure.....	367
Juice of Flesh.....	335	Bone-dust.....	367
Kreatine.....	336	Guano.....	367
Table of its amount in various kinds of Flesh and Fish.....	337	Phosphate of Lime.....	367
Lactic Acid.....	337	Fossil Guano.....	368
Inosinic Acid.....	338	Night Soil.—Urine.....	368
Phosphoric Acid.....	338	Rotation of Crops.....	368
Phosphate of Potash.....	338	Artificial Manures.....	369
Phosphate of Magnesia.....	338	Wood, Peat, and Coal Ashes.....	369
Saliva.....	339	Causes of Sterility in Soils.....	370
Pancreatic Juice.....	339	Dissolving Power of Carbonic Acid.....	370
Excrements, Urine.....	339	Effects of Light on Vegetation.....	371
Artificial Urine.....	339	Vegetables contain both non-nitrogenous or respiratory, and nitrogenous or sanguigenous food.....	371
Salts of Excreta, compared with those of Food.....	340	Food of Animals.....	372
Origin of the peculiar odor of Fæces.....	341	Digestion.....	372
Guano.....	341	Changes in the Animal Body.....	373
Theory of its actions.....	342	Urea in Animals.....	376
Urinary Calculi.....	342	Formation of Caseine from Albumen.....	377
Uric Acid.....	342	Components of Blood and Egg Albumen.....	377
Urate of Ammonia.....	343	Production of Fat from Sugar.....	378
Phosphate of Lime.....	343	Derivation of Fatty Acids from Sugar.....	380
Phosphate of Ammonia and Magnesia.....	343	Threefold Origin of Fat.....	381
Fusible Calculus.....	343	Different uses of Fat.....	381
Oxalate of Lime, or Mulberry Calculus.....	343	Process of Respiration.....	381
Carbonate of Lime.....	343	Pneumic Acid.....	382
Cystic Oxide, and Xanthic Oxide.....	343	Animal Heat.....	383
Lymph.....	343	Sanguigenous and Respiratory Food.....	384
Blood.....	343	Due Admixture of Food.....	385
Serum.....	343	Mineral Elements of Food.....	386
Globules.....	344	Ashes of Food.....	387
Coloring Matter.....	344	Soluble Salts in the Urine with different kinds of Food.....	388
Hematosine.....	345	Absolute Necessity of the use of different kinds of Food.....	388
Function of Phosphate of Soda in the Blood.....	346	Proper Method of Boiling Meat.....	389
NUTRITION OF PLANTS AND ANIMALS.....	346	Extract of Meat.....	389
Mineral Food of Plants.....	347	Importance of Salt.....	389
Process of Germination.....	347	Doctrine of Vegetarianism.....	390
Malate of Ammonia.—Malamide.....	348	Abuse of Fermented Liquors.....	390
Vegetative Process.....	348	Products of Decay.....	391
Decomposition of Carbonic Acid.....	348	Force from Food.....	392
Formation of Oxalic Acid.....	349	Causes of Disease.....	392
" Malic ".....	349	Insoluble Phosphates.....	393
Production of Tartaric and Citric Acids.....	349	Use of Iron as a Medicine.....	393
Formation of Glucose.....	350	Good effects of Cod-liver oil, and other fatty substances in chronic wasting diseases.....	394
Tabular View of the Production of Vegetable Compounds.....	350		

	PAGE		PAGE
Food of Children.—Use of Lime.....	394	Silicates of Oxide of Ethyle.....	437
Checked Perspiration.—Use of Purga- tives.....	394	Chlorocarbonic Ether.....	438
Use of Tea, Coffee, &c.....	394	Carbanic Ether, or Urethane.....	438
SUPPLEMENT.....	397	Cyanic Ether.....	438
Rapid Progress of Organic Chemistry.....	397	Ethilo-urea.....	438
Homologous Series of Organic Com- pounds.....	397	Allophanate of Oxide of Ethyle.....	439
Homologous Series of Alcohols.....	398	Cyanuric Ether.....	439
Analogy between certain Organic Compounds and some Elementary Bodies.....	404	Alcoholate of Potash.....	439
Affinity between Chlorine, Bromine, and Iodine.....	404	Bases containing Ethyle.....	440
Transmutation.....	405	Ethylamine.....	440
Alcaloids or Organic Bases.....	406	Diethylamine.....	442
Formation and Constitution of Arti- ficial Organic Bases.....	406	Triethylamine.....	443
Table of Amide Bases.....	409	Tetraethylum.....	443
“ “ Imide “.....	410	Methylotriethylum.....	443
“ “ Nitrile “.....	410	Acetylammionium.....	444
Ammonium Bases.....	411	Hydrated Oxide of Acetylammionium.....	444
Hydrated Oxides of Ammonium Bases.....	412	Benzole Compounds.....	446
Properties of Ammonium Bases.....	412	Table of Benzole Compounds.....	447
Methods employed for the produc- tion of Artificial Bases.....	413	New Class of Alcohols.....	448
Various Derivations from Ani- line.....	415	Table of the Allylic and Ethylic Series.....	450
Cyaniline.....	415	Table of Alcohols and their Derived Acids.....	451
Melaniline.....	415	New Class of Acids.....	451
Other Derivations from Aniline.....	417	Insolitic Acid.....	451
Methyle and Ethyle.....	418	New Phosphorised Acids.....	452
Carbonate of Oxide of Methyle.....	421	Trigenic Acid.....	453
Phenomethole.....	421	Sudoric Acid.....	453
Cyanate of Oxide of Methyle.....	422	Thylamine.....	454
Allophanate “ “.....	422	The Theories of Chemistry.....	454
Cyanurate “ “.....	422	Table of Radicals and their Derivatives.....	456
Methylamine.....	423	Action of Hyponitrous Acid on artificial bases.....	459
Methyloxamide.....	424	Propyle.....	460
Methyloxamic Acid.....	424	Propylamine.....	460
Dimethylamine.....	426	Propionyle.....	460
Trimethylamine.....	426	Propional.....	460
Tetramethylum.....	427	Hydrated Propylic Acid.....	460
Chloride of Tetramethylum.....	428	Propione.....	460
Zincmethyle.....	430	Propylamide.....	460
Stibiomethyle.....	430	Allyle.....	461
Stibiomethylum.....	430	Butyle.....	461
Alkarsine, or Liquor of Cadet.....	430	Butylamine—Butyryle.....	461
Chloroform, or Terechloride of Formyle.....	431	Amyle.....	461
Combinations of Ethile with metals, phosphorus &c.....	433	Caprotyle.....	461
Zyncethyle.....	433	Heptyle or Enanthyle.....	461
Stibethyle.....	433	Nenyle—Pelorgyle.....	462
Sulphide of Stibethyle.....	434	Capryle or Rutyle.....	462
Stibethylum.....	434	Cetyle—Palmityle.....	462
Bismethyles.....	434	Methylic Alcohol.....	463
Stannethyle.....	435	Penta-iodide of Tetramethylum.....	463
Arsenodimethyle.....	435	Deca-iodide of Tetramethylum.....	463
Arsenethylum.....	435	Action of Chlorine on Sulphocyanide of Methyle.....	463
Plumbethyle.....	435	Formation of Alcohol from O eflant Gas.....	464
Mercuriethyle.....	435	Preparation of Chloride of Ethylene.....	465
Tellurethyle.....	435	Compound Ethers.....	466
Perchloric Ether.....	436	Propylene.....	466
Borates of Oxide of Ethyle.....	437	Formation of Propylic Alcohol.....	467
		Butyle.....	468
		Ethylbutyle.....	468
		Ethyl-amyle, Butyl-amyle, &c.....	469
		Schweinfurt Green and Butyric Acid.....	470
		Alloxanic Acid.....	470









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